

17.0 Tables, Diagrams, Flowcharts, and Validation Data

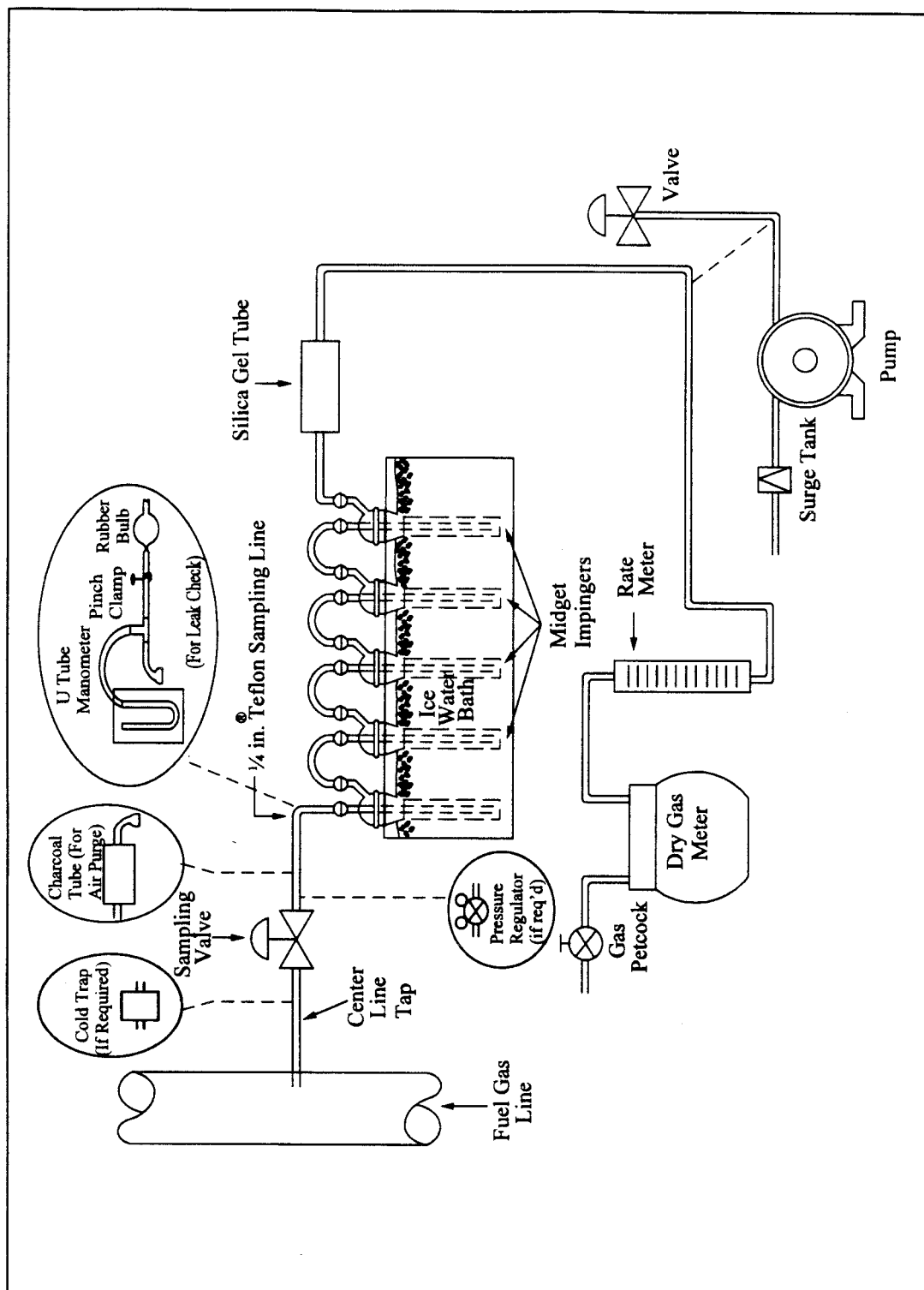


Figure 11-1. Hydrogen Sulfide Sampling Train.

Method 12—Determination of Inorganic Lead Emissions From Stationary Sources

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge

of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Application**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Inorganic Lead Compounds as lead (Pb)	7439-92-1	see Section 13.3.

1.2 Applicability. This method is applicable for the determination of inorganic lead emissions from stationary sources, only as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate and gaseous Pb emissions are withdrawn isokinetically from the source and are collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and are analyzed by atomic absorption spectrophotometry using an air/acetylene flame.

3.0 Definitions. [Reserved]**4.0 Interferences**

4.1 Copper. High concentrations of copper may interfere with the analysis of Pb at 217.0 nm. This interference can be avoided by analyzing the samples at 283.3 nm.

4.2 Matrix Effects. Analysis for Pb by flame atomic absorption spectrophotometry is sensitive to the chemical composition and to the physical properties (e.g., viscosity, pH) of the sample. The analytical procedure requires the use of the Method of Standard Additions to check for these matrix effects, and requires sample analysis using the Method of Standard Additions if significant matrix effects are found to be present.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing

chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H₂O₂). Irritating to eyes, skin, nose, and lungs.

5.2.2 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 12-1 in Section 18.0; it is similar to the Method 5 train. The following items are needed for sample collection:

6.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Temperature Sensor, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.1 through 6.1.1.7, 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.2 Impingers. Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings are needed. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip.

6.1.3 Temperature Sensor. Place a temperature sensor, capable of measuring temperature to within 1 °C (2 °F) at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber

Policeman. Same as Method 5, Sections 6.2.1 and 6.2.4 through 6.2.7, respectively.

6.2.2 Wash Bottles. Glass (2).

6.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for 0.1 N nitric acid (HNO₃) impinger and probe solutions and washes, 1000-ml. Use screw-cap liners that are either rubber-backed Teflon or leak-free and resistant to chemical attack by 0.1 N HNO₃. (Narrow mouth glass bottles have been found to be less prone to leakage.)

6.2.4 Funnel. Glass, to aid in sample recovery.

6.3 Sample Analysis. The following items are needed for sample analysis:

6.3.1 Atomic Absorption Spectrophotometer. With lead hollow cathode lamp and burner for air/acetylene flame.

6.3.2 Hot Plate.

6.3.3 Erlenmeyer Flasks. 125-ml, 24/40 standard taper.

6.3.4 Membrane Filters. Millipore SCWPO 4700, or equivalent.

6.3.5 Filtration Apparatus. Millipore vacuum filtration unit, or equivalent, for use with the above membrane filter.

6.3.6 Volumetric Flasks. 100-ml, 250-ml, and 1000-ml.

7.0 Reagents and Standards

Note: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are needed for sample collection:

7.1.1 Filter. Gelman Spectro Grade, Reeve Angel 934 AH, MSA 1106 BH, all with lot assay for Pb, or other high-purity glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. Conduct the filter efficiency test using ASTM D 2986-71, 78, or 95a (incorporated by reference—see § 60.17) or use test data from the supplier's quality control program.

7.1.2 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5,

Sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.3 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91, Type 3 (incorporated by reference—see § 60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.4 Nitric Acid, 0.1 N. Dilute 6.5 ml of concentrated HNO_3 to 1 liter with water. (It may be desirable to run blanks before field use to eliminate a high blank on test samples.)

7.2 Sample Recovery. 0.1 N HNO_3 (Same as in Section 7.1.4 above).

7.3 Sample Analysis. The following reagents and standards are needed for sample analysis:

7.3.1 Water. Same as in Section 7.1.3.

7.3.2 Nitric Acid, Concentrated.

7.3.3 Nitric Acid, 50 Percent (v/v). Dilute 500 ml of concentrated HNO_3 to 1 liter with water.

7.3.4 Stock Lead Standard Solution, 1000 $\mu\text{g Pb/ml}$. Dissolve 0.1598 g of lead nitrate [$\text{Pb}(\text{NO}_3)_2$] in about 60 ml water, add 2 ml concentrated HNO_3 , and dilute to 100 ml with water.

7.3.5 Working Lead Standards. Pipet 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the stock lead standard solution (Section 7.3.4) into 250-ml volumetric flasks. Add 5 ml of concentrated HNO_3 to each flask, and dilute to volume with water. These working standards contain 0.0, 4.0, 8.0, 12.0, 16.0, and 20.0 $\mu\text{g Pb/ml}$, respectively. Prepare, as needed, additional standards at other concentrations in a similar manner.

7.3.6 Air. Suitable quality for atomic absorption spectrophotometry.

7.3.7 Acetylene. Suitable quality for atomic absorption spectrophotometry.

7.3.8 Hydrogen Peroxide, 3 Percent (v/v). Dilute 10 ml of 30 percent H_2O_2 to 100 ml with water.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 8.1, except that the filter need not be weighed.

8.2 Preliminary Determinations. Follow the same general procedure given in Method 5, Section 8.2.

8.3 Preparation of Sampling Train. Follow the same general procedure given in Method 5, Section 8.3, except place 100 ml of 0.1 N HNO_3 (instead of water) in each of the first two impingers. As in Method 5, leave the third impinger empty and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Set up the train as shown in Figure 12-1.

8.4 Leak-Check Procedures. Same as Method 5, Section 8.4.

8.5 Sampling Train Operation. Same as Method 5, Section 8.5.

8.6 Calculation of Percent Isokinetic. Same as Method 5, Section 8.6.

8.7 Sample Recovery. Same as Method 5, Sections 8.7.1 through 8.7.6.1, with the addition of the following:

8.7.1 Container No. 2 (Probe).

8.7.1.1 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover sample matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 0.1 N HNO_3 and placing the wash into a glass sample storage container. Measure and record (to the nearest 2 ml) the total amount of 0.1 N HNO_3 used for these rinses. Perform the 0.1 N HNO_3 rinses as follows:

8.7.1.2 Carefully remove the probe nozzle, and rinse the inside surfaces with 0.1 N HNO_3 from a wash bottle while brushing with a stainless steel, Nylon-bristle brush. Brush until the 0.1 N HNO_3 rinse shows no visible particles, then make a final rinse of the inside surface with 0.1 N HNO_3 .

8.7.1.3 Brush and rinse with 0.1 N HNO_3 the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

8.7.1.4 Rinse the probe liner with 0.1 N HNO_3 . While rotating the probe so that all inside surfaces will be rinsed with 0.1 N HNO_3 , tilt the probe, and squirt 0.1 N HNO_3 into its upper end. Let the 0.1 N HNO_3 drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, squirt 0.1 N HNO_3 into the upper end of the probe as the probe brush is being pushed with a twisting action through the probe; hold the sample container underneath the lower end of the probe, and catch any 0.1 N HNO_3 and sample matter that is brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N HNO_3 and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which sample matter can be entrapped. Rinse the brush with 0.1 N HNO_3 , and quantitatively collect these washings in the sample container. After

the brushing, make a final rinse of the probe as described above.

8.7.1.5 It is recommended that two people clean the probe to minimize loss of sample. Between sampling runs, keep brushes clean and protected from contamination.

8.7.1.6 After ensuring that all joints are wiped clean of silicone grease, brush and rinse with 0.1 N HNO_3 the inside of the front half of the filter holder. Brush and rinse each surface three times or more, if needed, to remove visible sample matter. Make a final rinse of the brush and filter holder. After all 0.1 N HNO_3 washings and sample matter are collected in the sample container, tighten the lid on the sample container so that the fluid will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents clearly.

8.7.2 Container No. 3 (Silica Gel). Note the color of the indicating silica gel to determine if it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to the original container, and seal. A funnel may be used to pour the silica gel from the impinger and a rubber policeman may be used to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in Section 11.4.2.

8.7.3 Container No. 4 (Impingers). Due to the large quantity of liquid involved, the impinger solutions may be placed in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

8.7.3.1 Wipe the impinger ball joints free of silicone grease, and cap the joints.

8.7.3.2 Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

8.7.3.3 Transfer the contents of the impingers to a 500-ml graduated cylinder. Remove the outlet ball joint cap, and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within 2 ml. Alternatively, determine the weight of the liquid to within 0.5 g. Record in the log the volume or weight of the liquid present, along with a

notation of any color or film observed in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-6).

8.7.3.4. Transfer the contents to Container No. 4.

Note: In Sections 8.7.3.5 and 8.7.3.6, measure and record the total amount of 0.1 N HNO₃ used for rinsing.

8.7.3.5. Pour approximately 30 ml of 0.1 N HNO₃ into each of the first three impingers and agitate the impingers.

Drain the 0.1 N HNO₃ through the outlet arm of each impinger into Container No. 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

8.7.3.6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N HNO₃; transfer this rinse into Container No. 4. Do not rinse or brush the glass-fritted filter support. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents clearly.

8.8 Blanks.

8.8.1 Nitric Acid. Save 200 ml of the 0.1 N HNO₃ used for sampling and cleanup as a blank. Take the solution directly from the bottle being used and place into a glass sample container labeled "0.1 N HNO₃ blank."

8.8.2 Filter. Save two filters from each lot of filters used in sampling. Place these filters in a container labeled "filter blank."

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminate matrix effects.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardizations

Note: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Spectrophotometer.

10.2.1 Measure the absorbance of the standard solutions using the instrument settings recommended by the spectrophotometer manufacturer. Repeat until good agreement (± 3 percent) is obtained between two consecutive readings. Plot the absorbance (y-axis) versus concentration in $\mu\text{g Pb/ml}$ (x-axis). Draw or compute a straight line through the linear portion of the curve. Do not force the calibration curve through zero, but if the curve does not pass through the origin or at least lie closer to the origin than ± 0.003 absorbance units, check for incorrectly prepared standards and for curvature in the calibration curve.

10.2.2 To determine stability of the calibration curve, run a blank and a standard after every five samples, and recalibrate as necessary.

11.0 Analytical Procedures

11.1 Sample Loss Check. Prior to analysis, check the liquid level in Containers Number 2 and Number 4. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.

11.2 Sample Preparation.

11.2.1 Container No. 1 (Filter). Cut the filter into strips and transfer the

strips and all loose particulate matter into a 125-ml Erlenmeyer flask. Rinse the petri dish with 10 ml of 50 percent HNO₃ to ensure a quantitative transfer, and add to the flask.

Note: If the total volume required in Section 11.2.3 is expected to exceed 80 ml, use a 250-ml flask in place of the 125-ml flask.

11.2.2 Containers No. 2 and No. 4 (Probe and Impingers). Combine the contents of Containers No. 2 and No. 4, and evaporate to dryness on a hot plate.

11.2.3 Sample Extraction for Lead.
11.2.3.1 Based on the approximate stack gas particulate concentration and the total volume of stack gas sampled, estimate the total weight of particulate sample collected. Next, transfer the residue from Containers No. 2 and No. 4 to the 125-ml Erlenmeyer flask that contains the sampling filter using a rubber policeman and 10 ml of 50 percent HNO₃ for every 100 mg of sample collected in the train or a minimum of 30 ml of 50 percent HNO₃, whichever is larger.

11.2.3.2 Place the Erlenmeyer flask on a hot plate, and heat with periodic stirring for 30 minutes at a temperature just below boiling. If the sample volume falls below 15 ml, add more 50 percent HNO₃. Add 10 ml of 3 percent H₂O₂, and continue heating for 10 minutes. Add 50 ml of hot (80 °C, 176 °F) water, and heat for 20 minutes. Remove the flask from the hot plate, and allow to cool. Filter the sample through a Millipore membrane filter, or equivalent, and transfer the filtrate to a 250-ml volumetric flask. Dilute to volume with water.

11.2.4 Filter Blank. Cut each filter into strips, and place each filter in a separate 125-ml Erlenmeyer flask. Add

15 ml of 50 percent HNO₃, and treat as described in Section 11.2.3 using 10 ml of 3 percent H₂O₂ and 50 ml of hot water. Filter and dilute to a total volume of 100 ml using water.

11.2.5 Nitric Acid Blank, 0.1 N. Take the entire 200 ml of 0.1 N HNO₃ to dryness on a steam bath, add 15 ml of 50 percent HNO₃, and treat as described in Section 11.2.3 using 10 ml of 3 percent H₂O₂ and 50 ml of hot water. Dilute to a total volume of 100 ml using water.

11.3 Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current; and adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.4 Analysis.

11.4.1 Lead Determination. Calibrate the spectrophotometer as outlined in Section 10.2, and determine the absorbance for each source sample, the filter blank, and 0.1 N HNO₃ blank. Analyze each sample three times in this manner. Make appropriate dilutions, as needed, to bring all sample Pb concentrations into the linear absorbance range of the spectrophotometer. Because instruments vary between manufacturers, no detailed operating instructions will be given here. Instead, the instructions provided with the particular instrument should be followed. If the Pb concentration of a sample is at the low end of the calibration curve and high accuracy is required, the sample can be taken to dryness on a hot plate and the residue dissolved in the appropriate volume of water to bring it into the optimum range of the calibration curve.

11.4.2 Container No. 3 (Silica Gel). This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

11.5 Check for Matrix Effects. Use the Method of Standard Additions as follows to check at least one sample from each source for matrix effects on the Pb results:

11.5.1 Add or spike an equal volume of standard solution to an aliquot of the sample solution.

11.5.2 Measure the absorbance of the resulting solution and the absorbance of an aliquot of unspiked sample.

11.5.3 Calculate the Pb concentration C_m in $\mu\text{g}/\text{ml}$ of the sample solution using Equation 12-1 in Section 12.5.

Volume corrections will not be required if the solutions as analyzed have been made to the same final volume. Therefore, C_m and C_a represent Pb concentration before dilutions.

Method of Standard Additions procedures described on pages 9-4 and 9-5 of the section entitled "General Information" of the Perkin Elmer Corporation Atomic Absorption Spectrophotometry Manual, Number 303-0152 (Reference 1 in Section 17.0) may also be used. In any event, if the results of the Method of Standard Additions procedure used on the single source sample do not agree to within ± 5 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Standard Additions procedure.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A_m = Absorbance of the sample solution.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

A_t = Absorbance of the spiked sample solution.

B_{ws} = Water in the gas stream, proportion by volume.

C_a = Lead concentration in standard solution, $\mu\text{g}/\text{ml}$.

C_m = Lead concentration in sample solution analyzed during check for matrix effects, $\mu\text{g}/\text{ml}$.

C_s = Lead concentration in stack gas, dry basis, converted to standard conditions, mg/dscm (gr/dscf).

I = Percent of isokinetic sampling.

L_i = Individual leakage rate observed during the leak-check conducted prior to the first component change, m^3/min (ft^3/min)

L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to $0.00057 \text{ m}^3/\text{min}$

(0.020 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "ith" component change ($i = 1, 2, 3, \dots, n$), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

m_t = Total weight of lead collected in the sample, μg .

M_w = Molecular weight of water, 18.0 g/g-mole ($18.0 \text{ lb}/\text{lb-mole}$).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, $0.06236 [(\text{mm Hg})/[(^\circ\text{K}) (\text{g-mole})]] \{21.85 [(\text{in. Hg})/[(^\circ\text{R}) (\text{lb-mole})]]\}$.

T_m = Absolute average dry gas meter temperature (see Figure 5-3 of Method 5), $^\circ\text{K}$ ($^\circ\text{R}$).

T_{std} = Standard absolute temperature, $293 \text{ }^\circ\text{K}$ ($528 \text{ }^\circ\text{R}$).

v_s = Stack gas velocity, m/sec (ft/sec).

V_m = Volume of gas sample as measured by the dry gas meter, dry basis, m^3 (ft^3).

$V_{m(\text{std})}$ = Volume of gas sample as measured by the dry gas meter, corrected to standard conditions, m^3 (ft^3).

$V_{w(\text{std})}$ = Volume of water vapor collected in the sampling train, corrected to standard conditions, m^3 (ft^3).

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5-3 of Method 5), $\text{mm H}_2\text{O}$ ($\text{in. H}_2\text{O}$).

θ = Total sampling time, min .

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min .

θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min .

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min .

ρ_w = Density of water, $0.9982 \text{ g}/\text{ml}$ ($0.002201 \text{ lb}/\text{ml}$).

12.2 Average Dry Gas Meter Temperatures (T_m) and Average Orifice Pressure Drop (ΔH). See data sheet (Figure 5-3 of Method 5).

12.3 Dry Gas Volume, Volume of Water Vapor, and Moisture Content. Using data obtained in this test, calculate $V_{m(\text{std})}$, $V_{w(\text{std})}$, and B_{ws} according to the procedures outlined in Method 5, Sections 12.3 through 12.5.

12.4 Total Lead in Source Sample. For each source sample, correct the

average absorbance for the contribution of the filter blank and the 0.1 N HNO_3 blank. Use the calibration curve and this corrected absorbance to determine the Pb concentration in the sample aspirated into the spectrophotometer. Calculate the total Pb content m_t (μg) in the original source sample; correct for all the dilutions that were made to bring the Pb concentration of the sample into the linear range of the spectrophotometer.

12.5 Sample Lead Concentration. Calculate the Pb concentration of the sample using the following equation:

$$C_m = C_a \frac{A_m}{A_t - A_m} \quad \text{Eq. 12-1}$$

12.6 Lead Concentration. Calculate the stack gas Pb concentration C_s using Equation 12-2:

$$C_s = K_3 \frac{m_t}{V_{m(\text{std})}} \quad \text{Eq. 12-2}$$

Where:

$K_3 = 0.001 \text{ mg}/\mu\text{g}$ for metric units.
 $= 1.54 \times 10^{-5} \text{ gr}/\mu\text{g}$ for English units

12.7 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate using data obtained in this method and the equations in Sections 12.2 and 12.3 of Method 2.

12.8 Isokinetic Variation. Same as Method 5, Section 12.11.

13.0 Method Performance

13.1 Precision. The within-laboratory precision, as measured by the coefficient of variation, ranges from 0.2 to 9.5 percent relative to a run-mean concentration. These values were based on tests conducted at a gray iron foundry, a lead storage battery manufacturing plant, a secondary lead smelter, and a lead recovery furnace of an alkyl lead manufacturing plant. The concentrations encountered during these tests ranged from 0.61 to $123.3 \text{ mg Pb}/\text{m}^3$.

13.2 Analytical Range. For a minimum analytical accuracy of ± 10 percent, the lower limit of the range is $100 \mu\text{g}$. The upper limit can be extended considerably by dilution.

13.3 Analytical Sensitivity. Typical sensitivities for a 1-percent change in absorption (0.0044 absorbance units) are 0.2 and $0.5 \mu\text{g Pb}/\text{ml}$ for the 217.0 and 283.3 nm lines, respectively.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

16.1 Simultaneous Determination of Particulate and Lead Emissions. Method

5 may be used to simultaneously determine Pb provided: (1) acetone is used to remove particulate from the probe and inside of the filter holder as specified by Method 5, (2) 0.1 N HNO₃ is used in the impingers, (3) a glass fiber filter with a low Pb background is used, and (4) the entire train contents, including the impingers, are treated and analyzed for Pb as described in Sections 8.0 and 11.0 of this method.

16.2 Filter Location. A filter may be used between the third and fourth impingers provided the filter is included in the analysis for Pb.

16.3 In-Stack Filter. An in-stack filter may be used provided: (1) A glass-

lined probe and at least two impingers, each containing 100 ml of 0.1 N HNO₃ after the in-stack filter, are used and (2) the probe and impinger contents are recovered and analyzed for Pb. Recover sample from the nozzle with acetone if a particulate analysis is to be made.

17.0 References

Same as Method 5, Section 17.0, References 2, 3, 4, 5, and 7, with the addition of the following:

1. Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, Connecticut. September 1976.

2. American Society for Testing and Materials. Annual Book of ASTM Standards, Part 31: Water, Atmospheric Analysis. Philadelphia, PA 1974. p. 40–42.

3. Kelen, R., and C. Hach. Standard Additions—Uses and Limitations in Spectrophotometric Analysis. Amer. Lab. 9:21–27. 1977.

4. Mitchell, W.J., and M.R. Midgett. Determining Inorganic and Alkyl Lead Emissions from Stationary Sources. U.S. Environmental Protection Agency. Emission Monitoring and Support Laboratory. Research Triangle Park, NC. (Presented at National APCA Meeting, Houston. June 26, 1978).

BILLING CODE 6560–50–P

18.0 Tables, Diagrams, Flowcharts, and Validation Data

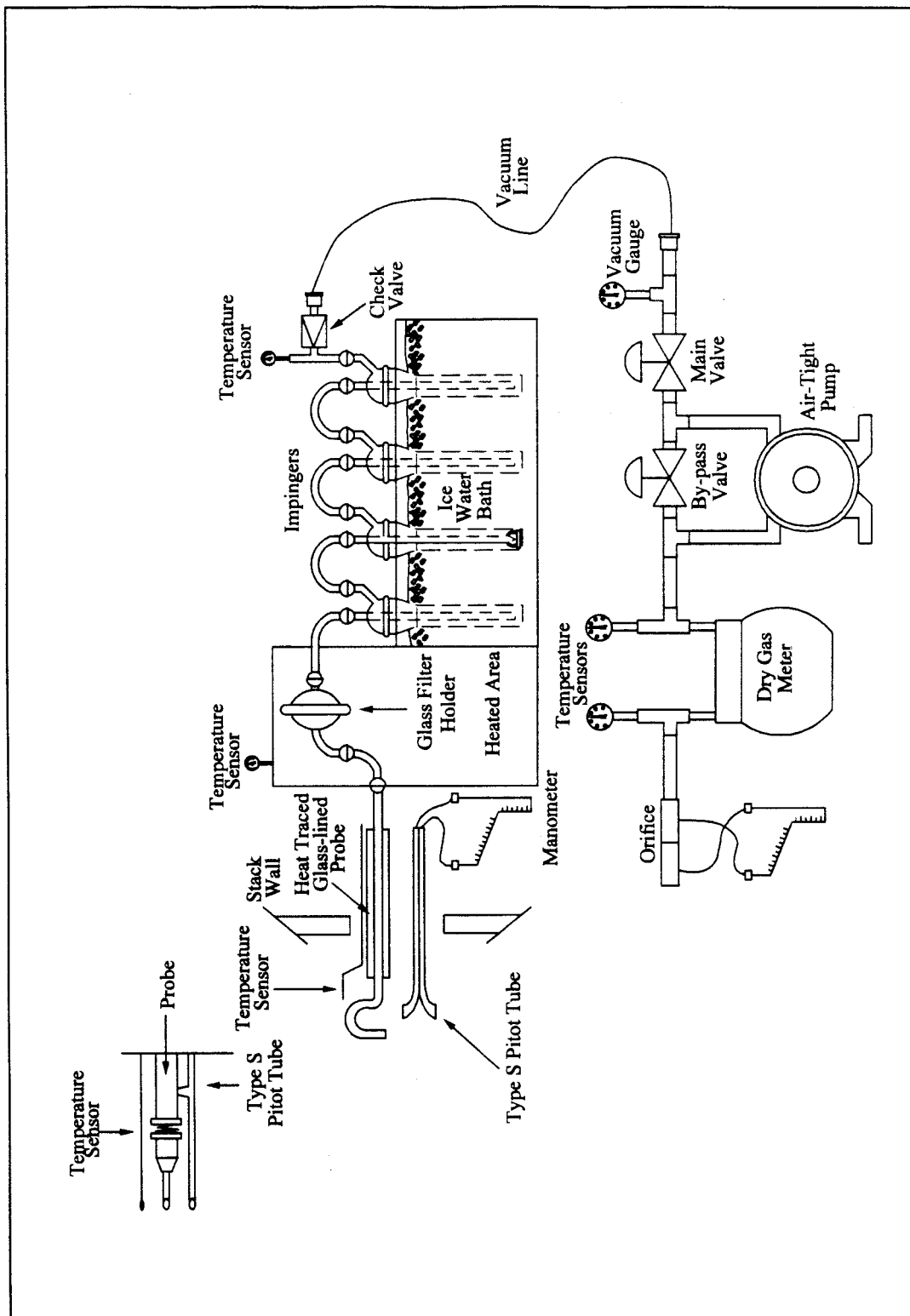


Figure 12-1. Inorganic Lead Sampling Train.

Method 13A—Determination of Total Fluoride Emissions From Stationary Sources (Spadns Zirconium Lake Method)

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 2, Method 3, and Method 5.

1.0 Scope and Application**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine	7782-41-4	Not determined.

1.2 Applicability. This method is applicable for the determination of fluoride (F^-) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary

Gaseous and particulate F^- are withdrawn isokinetically from the source and collected in water and on a filter. The total F^- is then determined by the SPADNS Zirconium Lake Colorimetric method.

3.0 Definitions [Reserved]**4.0 Interferences**

4.1 Chloride. Large quantities of chloride will interfere with the analysis, but this interference can be prevented by adding silver sulfate into the distillation flask (see Section 11.3). If chloride ion is present, it may be easier to use the specific ion electrode method of analysis (Method 13B).

4.2 Grease. Grease on sample-exposed surfaces may cause low F^- results due to adsorption.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/ m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 13A-1; it is similar to the Method 5 sampling train except that the filter position is interchangeable. The sampling train consists of the following components:

6.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Heating System, Temperature Sensor, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 6.1.1.1, 6.1.1.3 through 6.1.1.7, 6.1.1.9, 6.1.2, and 6.1.3, respectively. The filter heating system and temperature sensor are needed only when moisture condensation is a problem.

6.1.2 Probe Liner. Borosilicate glass or 316 stainless steel. When the filter is located immediately after the probe, a probe heating system may be used to prevent filter plugging resulting from moisture condensation, but the temperature in the probe shall not be allowed to exceed $120 \pm 14^\circ C$ ($248 \pm 25^\circ F$).

6.1.3 Filter Holder. With positive seal against leakage from the outside or around the filter. If the filter is located between the probe and first impinger, use borosilicate glass or stainless steel with a 20-mesh stainless steel screen filter support and a silicone rubber gasket; do not use a glass frit or a sintered metal filter support. If the filter is located between the third and fourth impingers, borosilicate glass with a glass frit filter support and a silicone rubber gasket may be used. Other materials of construction may be used, subject to the approval of the Administrator.

6.1.4 Impingers. Four impingers connected as shown in Figure 13A-1 with ground-glass (or equivalent), vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm ($\frac{1}{2}$ in.) ID glass tube extending to 1.3 cm ($\frac{1}{2}$ in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Modifications (e.g., flexible connections between the impingers or materials other than glass) may be used, subject to the approval of the Administrator. Place a temperature sensor, capable of measuring temperature to within $1^\circ C$ ($2^\circ F$), at the outlet of the fourth impinger for monitoring purposes.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe-liner and Probe-Nozzle Brushes, Wash Bottles, Graduated Cylinder and/or Balance, Plastic Storage Containers, Funnel and Rubber Policeman, and Funnel. Same as Method 5, Sections 6.2.1, 6.2.2 and 6.2.5 to 6.2.8, respectively.

6.2.2 Sample Storage Container. Wide-mouth, high-density polyethylene bottles for impinger water samples, 1 liter.

6.3 Sample Preparation and Analysis. The following items are needed for sample preparation and analysis:

6.3.1 Distillation Apparatus. Glass distillation apparatus assembled as shown in Figure 13A-2.

6.3.2 Bunsen Burner.

6.3.3 Electric Muffle Furnace. Capable of heating to 600 °C (1100 °F).
6.3.4 Crucibles. Nickel, 75- to 100-ml.

6.3.5 Beakers. 500-ml and 1500-ml.

6.3.6 Volumetric Flasks. 50-ml.

6.3.7 Erlenmeyer Flasks or Plastic Bottles. 500-ml.

6.3.8 Constant Temperature Bath. Capable of maintaining a constant temperature of ± 1.0 °C at room temperature conditions.

6.3.9 Balance. 300-g capacity, to measure to ± 0.5 g.

6.3.10 Spectrophotometer. Instrument that measures absorbance at 570 nm and provides at least a 1-cm light path.

6.3.11 Spectrophotometer Cells. 1-cm path length.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are needed for sample collection:

7.1.1 Filters.

7.1.1.1 If the filter is located between the third and fourth impingers, use a Whatman No. 1 filter, or equivalent, sized to fit the filter holder.

7.1.1.2 If the filter is located between the probe and first impinger, use any suitable medium (e.g., paper, organic membrane) that can withstand prolonged exposure to temperatures up to 135 °C (275 °F), and has at least 95 percent collection efficiency (<5 percent penetration) for 0.3 μ m dioctyl phthalate smoke particles. Conduct the filter efficiency test before the test series, using ASTM D 2986-71, 78, or 95a (incorporated by reference—see § 60.17), or use test data from the supplier's quality control program. The filter must also have a low F^- blank value (<0.015 mg F^- /cm² of filter area). Before the test series, determine the average F^- blank value of at least three filters (from the lot to be used for sampling) using the applicable procedures described in Sections 8.3 and 8.4 of this method. In general, glass fiber filters have high and/or variable F^- blank values, and will not be acceptable for use.

7.1.2 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91, Type 3 (incorporated by reference—see § 60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be deleted.

7.1.3 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.2 Sample Recovery. Water, as described in Section 7.1.2, is needed for sample recovery.

7.3 Sample Preparation and Analysis. The following reagents and standards are needed for sample preparation and analysis:

7.3.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F^- or less.

7.3.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml of water.

7.3.3 Silver Sulfate (Ag_2SO_4).

7.3.4 Sodium Hydroxide (NaOH), Pellets.

7.3.5 Sulfuric Acid (H_2SO_4), Concentrated.

7.3.6 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H_2SO_4 with 3 parts of water.

7.3.7 Filters. Whatman No. 541, or equivalent.

7.3.8 Hydrochloric Acid (HCl), Concentrated.

7.3.9 Water. Same as in Section 7.1.2.

7.3.10 Fluoride Standard Solution, 0.01 mg F^- /ml. Dry approximately 0.5 g of sodium fluoride (NaF) in an oven at 110 °C (230 °F) for at least 2 hours. Dissolve 0.2210 g of NaF in 1 liter of water. Dilute 100 ml of this solution to 1 liter with water.

7.3.11 SPADNS Solution [4,5 Dihydroxyl-3-(p-Sulfophenylazo)-2,7-Naphthalene-Disulfonic Acid Trisodium Salt]. Dissolve 0.960 \pm 0.010 g of SPADNS reagent in 500 ml water. If stored in a well-sealed bottle protected from the sunlight, this solution is stable for at least 1 month.

7.3.12 Spectrophotometer Zero Reference Solution. Add 10 ml of SPADNS solution to 100 ml of water, and acidify with a solution prepared by diluting 7 ml of concentrated HCl to 10 ml with deionized, distilled water. Prepare daily.

7.3.13 SPADNS Mixed Reagent. Dissolve 0.135 \pm 0.005 g of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in 25 ml of water. Add 350 ml of concentrated HCl, and dilute to 500 ml with deionized, distilled water. Mix equal volumes of this solution and SPADNS solution to form a single reagent. This reagent is stable for at least 2 months.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Follow the general procedure given in Method 5,

Section 8.1, except that the filter need not be weighed.

8.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 8.2, except that the nozzle size must be selected such that isokinetic sampling rates below 28 liters/min (1.0 cfm) can be maintained.

8.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, Section 8.3, except for the following variation: Assemble the train as shown in Figure 13A-1 with the filter between the third and fourth impingers. Alternatively, if a 20-mesh stainless steel screen is used for the filter support, the filter may be placed between the probe and first impinger. A filter heating system to prevent moisture condensation may be used, but shall not allow the temperature to exceed 120 ± 14 °C (248 ± 25 °F). Record the filter location on the data sheet (see Section 8.5).

8.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 8.4.

8.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5, keeping the filter and probe temperatures (if applicable) at 120 ± 14 °C (248 ± 25 °F) and isokinetic sampling rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-3.

8.6 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.6.1 When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle, and place a cap over it to keep from losing part of the sample. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

8.6.2 Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Remove the filter assembly, wipe off any silicone grease from the filter holder inlet, and cap this inlet. Remove the umbilical cord from the last impinger, and cap the impinger. After wiping off any silicone grease, cap off the filter holder outlet and any open impinger inlets and outlets. Ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.6.3 Transfer the probe and filter-impinger assembly to the cleanup area.

This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.6.4 Inspect the train prior to and during disassembly, and note any abnormal conditions. Treat the samples as follows:

8.6.4.1 Container No. 1 (Probe, Filter, and Impinger Catches).

8.6.4.1.1 Using a graduated cylinder, measure to the nearest ml, and record the volume of the water in the first three impingers; include any condensate in the probe in this determination.

Transfer the impinger water from the graduated cylinder into a polyethylene container. Add the filter to this container. (The filter may be handled separately using procedures subject to the Administrator's approval.) Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all sample-exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder) with water. Use less than 500 ml for the entire wash. Add the washings to the sample container. Perform the water rinses as follows:

8.6.4.1.2 Carefully remove the probe nozzle and rinse the inside surface with water from a wash bottle. Brush with a Nylon bristle brush, and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with water in a similar way.

8.6.4.1.3 Rinse the probe liner with water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water

drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

8.6.4.1.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.6.4.1.5 Rinse the inside surface of each of the first three impingers (and connecting glassware) three separate times. Use a small portion of water for each rinse, and brush each sample-exposed surface with a Nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush.

8.6.4.1.6 After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with water the inside of the filter holder (front-half only, if filter is positioned

between the third and fourth impingers). Brush and rinse each surface three times or more if needed. Make a final rinse of the brush and filter holder.

8.6.4.1.7 After all water washings and particulate matter have been collected in the sample container, tighten the lid so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to transport. Label the container clearly to identify its contents.

8.6.4.2 Container No. 2 (Sample Blank). Prepare a blank by placing an unused filter in a polyethylene container and adding a volume of water equal to the total volume in Container No. 1. Process the blank in the same manner as for Container No. 1.

8.6.4.3 Container No. 3 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container, and seal. A funnel may be used to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the analytical procedure for Container No. 3 in Section 11.4.2.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.4, 10.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate and sample volume.
10.2	Spectrophotometer calibration	Evaluate analytical technique, preparation of standards.
11.3.3	Interference/recovery efficiency check during distillation.	Minimize negative effects of used acid.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardization

Note: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Calibrate the probe nozzle, pitot tube, metering system, probe heater, temperature sensors, and barometer according to the procedures outlined in Method 5, Sections 10.1 through 10.6. Conduct the leak-check of the metering system

according to the procedures outlined in Method 5, Section 8.4.1.

10.2 Spectrophotometer.

10.2.1 Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of water.

10.2.2 Accurately prepare a series of standards from the 0.01 mg F⁻/ml standard fluoride solution (Section 7.3.10) by diluting 0, 2, 4, 6, 8, 10, 12, and 14 ml to 100 ml with deionized, distilled water. Pipet 50 ml from each solution, and transfer each to a separate 100-ml beaker. Then add 10 ml of

SPADNS mixed reagent (Section 7.3.13) to each. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 µg F⁻ (0 to 1.4 µg/ml), respectively.

10.2.3 After mixing, place the blank and calibration standards in a constant temperature bath for 30 minutes before reading the absorbance with the spectrophotometer. Adjust all samples to this same temperature before analyzing.

10.2.4 With the spectrophotometer at 570 nm, use the blank standard to set

the absorbance to zero. Determine the absorbance of the standards.

10.2.5 Prepare a calibration curve by plotting $\mu\text{g F}^-$ /50 ml versus absorbance on linear graph paper. Prepare the standard curve initially and thereafter whenever the SPADNS mixed reagent is newly made. Also, run a calibration standard with each set of samples and, if it differs from the calibration curve by more than ± 2 percent, prepare a new standard curve.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the liquid levels in Containers No. 1 and No. 2, determine whether leakage occurred during transport, and note this finding on the analytical data sheet. If noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Treat the contents of each sample container as described below:

11.2.1 Container No. 1 (Probe, Filter, and Impinger Catches). Filter this container's contents, including the sampling filter, through Whatman No. 541 filter paper, or equivalent, into a 1500-ml beaker.

11.2.1.1 If the filtrate volume exceeds 900 ml, make the filtrate basic (red to phenolphthalein) with NaOH, and evaporate to less than 900 ml.

11.2.1.2 Place the filtered material (including sampling filter) in a nickel crucible, add a few ml of water, and macerate the filters with a glass rod.

11.2.1.2.1 Add 100 mg CaO to the crucible, and mix the contents thoroughly to form a slurry. Add two drops of phenolphthalein indicator. Place the crucible in a hood under infrared lamps or on a hot plate at low heat. Evaporate the water completely. During the evaporation of the water, keep the slurry basic (red to phenolphthalein) to avoid loss of F^- . If the indicator turns colorless (acidic) during the evaporation, add CaO until the color turns red again.

11.2.1.2.2 After evaporation of the water, place the crucible on a hot plate under a hood, and slowly increase the temperature until the Whatman No. 541 and sampling filters char. It may take several hours to char the filters completely.

11.2.1.2.3 Place the crucible in a cold muffle furnace. Gradually (to prevent smoking) increase the temperature to 600 °C (1100 °F), and maintain this temperature until the contents are reduced to an ash. Remove the crucible from the furnace, and allow to cool.

11.2.1.2.4 Add approximately 4 g of crushed NaOH to the crucible, and mix.

Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 600 °C.

11.2.1.2.5 Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm water, transfer the contents of the crucible to the beaker containing the filtrate. To ensure complete sample removal, rinse finally with two 20-ml portions of 25 percent H_2SO_4 , and carefully add to the beaker. Mix well, and transfer to a 1-liter volumetric flask. Dilute to volume with water, and mix thoroughly. Allow any undissolved solids to settle.

11.2.2 Container No. 2 (Sample Blank). Treat in the same manner as described in Section 11.2.1 above.

11.2.3 Adjustment of Acid/Water Ratio in Distillation Flask. Place 400 ml of water in the distillation flask, and add 200 ml of concentrated H_2SO_4 . Add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175 °C (347 °F) to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

Caution: Use a protective shield when carrying out this procedure. Observe standard precautions when mixing H_2SO_4 with water. Slowly add the acid to the flask with constant swirling.

11.3 Distillation.

11.3.1 Cool the contents of the distillation flask to below 80 °C (180 °F). Pipet an aliquot of sample containing less than 10.0 mg F^- directly into the distillation flask, and add water to make a total volume of 220 ml added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution, and treat as described in Section 11.4.1. This will be an approximation of the F^- content because of possible interfering ions.)

Note: If the sample contains chloride, add 5 mg of Ag_2SO_4 to the flask for every mg of chloride.

11.3.2 Place a 250-ml volumetric flask at the condenser exit. Heat the flask as rapidly as possible with a Bunsen burner, and collect all the distillate up to 175 °C (347 °F). During heatup, play the burner flame up and down the side of the flask to prevent bumping. Conduct the distillation as rapidly as possible (15 minutes or less). Slow distillations have been found to produce low F^- recoveries. Be careful not to exceed 175 °C (347 °F) to avoid causing H_2SO_4 to distill over. If F^- distillation in the mg range is to be followed by a distillation in the fractional mg range, add 220 ml of water and distill it over as in the acid

adjustment step to remove residual F^- from the distillation system.

11.3.3 The acid in the distillation flask may be used until there is carry-over of interferences or poor F^- recovery. Check for interference and for recovery efficiency every tenth distillation using a water blank and a standard solution. Change the acid whenever the F^- recovery is less than 90 percent or the blank value exceeds 0.1 $\mu\text{g/ml}$.

11.4 Sample Analysis.

11.4.1 Containers No. 1 and No. 2.

11.4.1.1 After distilling suitable aliquots from Containers No. 1 and No. 2 according to Section 11.3, dilute the distillate in the volumetric flasks to exactly 250 ml with water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to 40 $\mu\text{g F}^-/\text{ml}$) into a beaker, and dilute to 50 ml with water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (Section 7.3.13), and mix thoroughly.

11.4.1.2 After mixing, place the sample in a constant-temperature bath containing the standard solutions for 30 minutes before reading the absorbance on the spectrophotometer.

Note: After the sample and colorimetric reagent are mixed, the color formed is stable for approximately 2 hours. Also, a 3 °C (5.4 °F) temperature difference between the sample and standard solutions produces an error of approximately 0.005 mg F^-/liter . To avoid this error, the absorbencies of the sample and standard solutions must be measured at the same temperature.

11.4.1.3 Set the spectrophotometer to zero absorbance at 570 nm with the zero reference solution (Section 7.3.12), and check the spectrophotometer calibration with the standard solution (Section 7.3.10). Determine the absorbance of the samples, and determine the concentration from the calibration curve. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.

11.4.2 Container No. 3 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation. Other forms of the equations may be used, provided that they yield equivalent results.

12.1 Nomenclature.

A_d = Aliquot of distillate taken for color development, ml.

A_t = Aliquot of total sample added to still, ml.

B_{ws} = Water vapor in the gas stream, portion by volume.

C_s = Concentration of F^- in stack gas, mg/dscm (gr/dscf).

F_c = F^- concentration from the calibration curve, μg .

F_t = Total F^- in sample, mg.

T_m = Absolute average dry gas meter (DGM) temperature (see Figure 5-3 of Method 5), $^{\circ}K$ ($^{\circ}R$).

T_s = Absolute average stack gas temperature (see Figure 5-3 of Method 5), $^{\circ}K$ ($^{\circ}R$).

V_d = Volume of distillate as diluted, ml.

$V_{m(std)}$ = Volume of gas sample as measured by DGM at standard conditions, dscm (dscf).

V_t = Total volume of F^- sample, after final dilution, ml.

$V_{w(std)}$ = Volume of water vapor in the gas sample at standard conditions, scm (scf)

12.2 Average DGM Temperature and Average Orifice Pressure Drop (see Figure 5-3 of Method 5).

12.3 Dry Gas Volume. Calculate $V_{m(std)}$, and adjust for leakage, if necessary, using Equation 5-1 of Method 5.

12.4 Volume of Water Vapor and Moisture Content. Calculate $V_{w(std)}$ and B_{ws} from the data obtained in this

method. Use Equations 5-2 and 5-3 of Method 5.

12.5 Total Fluoride in Sample. Calculate the amount of F^- in the sample using the following equation:

$$F_t = \frac{K V_t V_d F_c}{A_t A_d} \quad \text{Eq. 13A-1}$$

Where:

$K = 10^{-3}$ mg/ μg (metric units)
 $= 1.54 \times 10^{-5}$ gr/ μg (English units)

12.6 Fluoride Concentration in Stack Gas. Determine the F^- concentration in the stack gas using the following equation:

$$C_f = \frac{F_t}{V_{m(std)}} \quad \text{Eq. 13A-2}$$

12.7 Isokinetic Variation. Same as Method 5, Section 12.11.

13.0 Method Performance

The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F^- /m³.

13.1 Precision. The intra- and inter-laboratory standard deviations, which include sampling and analysis errors, were 0.044 mg F^- /m³ with 60 degrees

of freedom and 0.064 mg F^- /m³ with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0 to 1.4 μg F^- /ml.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

16.1 Compliance with ASTM D 3270-73T, 80, 91, or 95 (incorporated by reference—see § 60.17) "Analysis of Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)" is an acceptable alternative for the requirements specified in Sections 11.2, 11.3, and 11.4.1 when applied to suitable aliquots of Containers 1 and 2 samples.

17.0 References

1. Bellack, Ervin. Simplified Fluoride Distillation Method. J. of the American Water Works Association. 50:5306. 1958.
2. Mitchell, W.J., J.C. Suggs, and F.J. Bergman. Collaborative Study of EPA Method 13A and Method 13B. Publication No. EPA-300/4-77-050. U.S. Environmental Protection Agency, Research Triangle Park, NC. December 1977.
3. Mitchell, W.J., and M.R. Midgett. Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride. Atm. Environ. 10:865-872. 1976.

BILLING CODE 6560-50-P

18.0 Tables, Diagrams, Flowcharts, and Validation Data

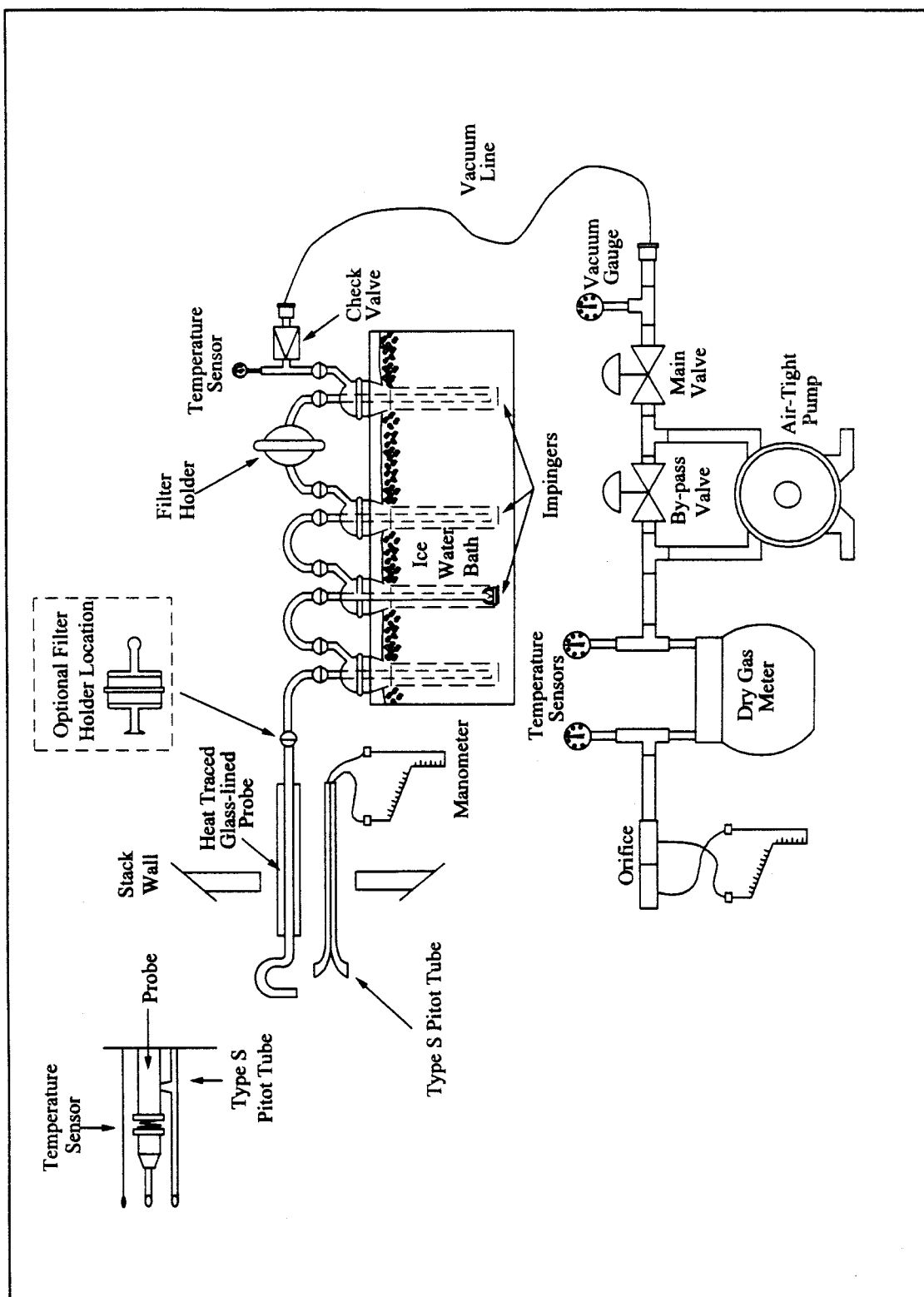


Figure 13A-1. Fluoride Sampling Train.

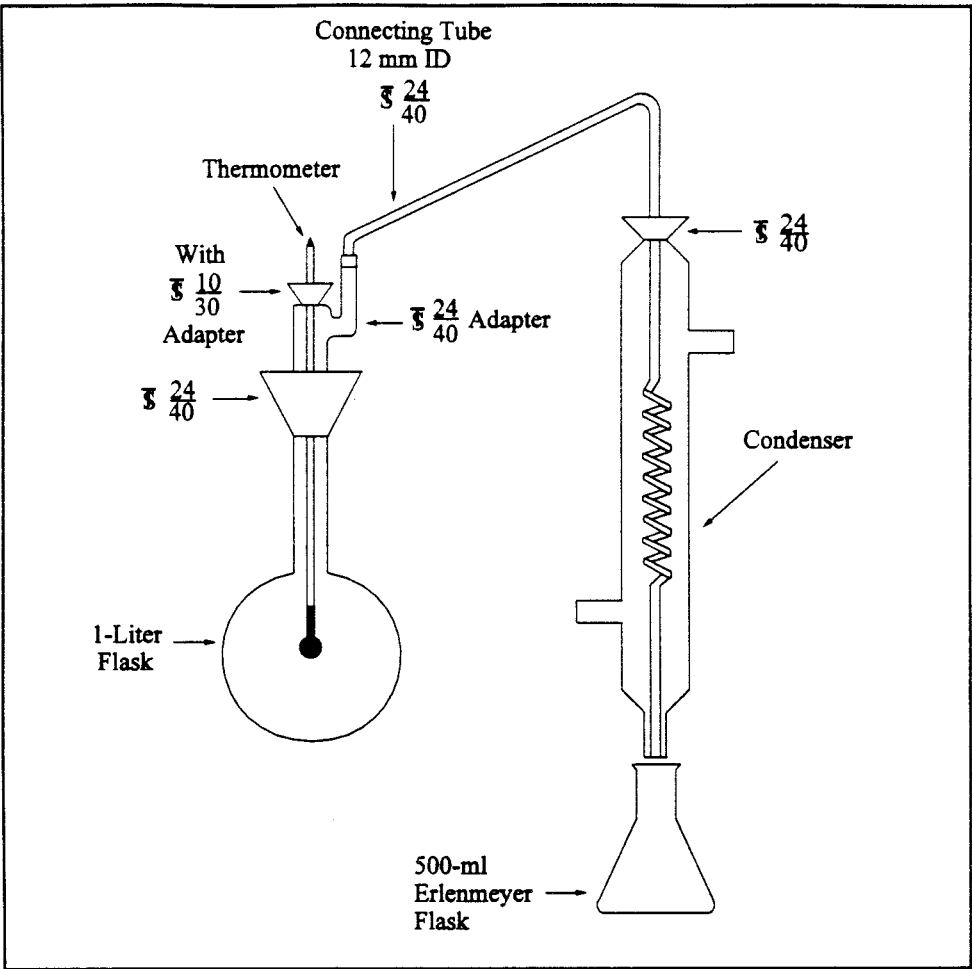


Figure 13A-2. Fluoride Distillation Apparatus.

BILLING CODE 6560-50-C

Method 13B—Determination of Total Fluoride Emissions From Stationary Sources (Specific Ion Electrode Method)

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 2, Method 3, Method 5, and Method 13A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine	7782-41-4	Not determined.

1.2 Applicability. This method is applicable for the determination of fluoride (F⁻) emissions from sources as specified in the regulations. It does not measure fluorocarbons, such as Freons.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary

Gaseous and particulate F⁻ are withdrawn isokinetically from the source and collected in water and on a

filter. The total F⁻ is then determined by the specific ion electrode method.

3.0 Definitions. [Reserved]

4.0 Interferences

Grease on sample-exposed surfaces may cause low F⁻ results because of adsorption.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is

the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and

decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H₂SO₄). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 13A, Sections 6.1 and 6.2, respectively.

6.2 Sample Preparation and Analysis. The following items are required for sample preparation and analysis:

6.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, Sections 6.3.1 to 6.3.9, respectively.

6.2.2 Fluoride Ion Activity Sensing Electrode.

6.2.3 Reference Electrode. Single junction, sleeve type.

6.2.4 Electrometer. A pH meter with millivolt-scale capable of ± 0.1 -mv resolution, or a specific ion meter made specifically for specific ion electrode use.

6.2.5 Magnetic Stirrer and Tetrafluoroethylene (TFE) Fluorocarbon-Coated Stirring Bars.

6.2.6 Beakers. Polyethylene, 100-ml.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection and Sample Recovery. Same as Method 13A, Sections 7.1 and 7.2, respectively.

7.2 Sample Preparation and Analysis. The following reagents and standards are required for sample analysis:

7.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F⁻ or less.

7.2.2 Phenolphthalein Indicator. Dissolve 0.1 g phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml water.

7.2.3 Sodium Hydroxide (NaOH), Pellets.

7.2.4 Sulfuric Acid (H₂SO₄), Concentrated.

7.2.5 Filters. Whatman No. 541, or equivalent.

7.2.6 Water. Same as Section 7.1.2 of Method 13A.

7.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of water.

7.2.8 Sulfuric Acid, 25 Percent (v/v). Mix 1 part of concentrated H₂SO₄ with 3 parts of water.

7.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath and cool to 20 °C (68 °F). Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Pour into a 1-liter volumetric flask, and dilute to volume with deionized, distilled water. Commercially prepared TISAB may be substituted for the above.

7.2.10 Fluoride Standard Solution, 0.1 M. Oven dry approximately 10 g of sodium fluoride (NaF) for a minimum of 2 hours at 110 °C (230 °F), and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough water to dissolve. Dilute to volume with water.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 13A, Section 8.0.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate and sample volume.
10.2	Fluoride electrode	Evaluate analytical technique, preparation of standards.
11.1	Interference/recovery efficiency-check during distillation.	Minimize negative effects of used acid.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardizations

Note: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 13A, Section 10.1.

10.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with water for a 10⁻² M standard solution. Use 10 ml of 10⁻² M solution to make a 10⁻³ M solution in the same manner. Repeat the dilution procedure, and make 10⁻⁴ and 10⁻⁵ M solutions.

10.2.1 Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, (e.g., when 50 ml of 10⁻² M standard is diluted with 50 ml of TISAB, the concentration is still designated "10⁻² M").

10.2.2 Between measurements, soak the fluoride sensing electrode in water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be

obtained, with nominal concentrations of 10⁻⁴, 10⁻³, 10⁻², 10⁻¹ fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between 10⁻⁵ and 10⁻⁴ M. If this occurs, use additional standards between these two concentrations.

10.2.3 Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10⁻² M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

Note: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride

measurements over a narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.

11.0 Analytical Procedures

11.1 Sample Loss Check, Sample Preparation, and Distillation. Same as Method 13A, Sections 11.1 through 11.3, except that the **Note** following Section 11.3.1 is not applicable.

11.2 Analysis.
11.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with water, and mix thoroughly. Pipet a 25-ml aliquot from each of the distillate into separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than ±2 °C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material, such as cork, between the stirrer and the beaker. Hold dilute samples (below 10⁻⁴ M fluoride ion content) in polyethylene beakers during measurement.

11.2.2 Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with water.

11.2.3 Container No. 3 (Silica Gel). Same as in Method 13A, Section 11.4.2.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 13A, Section 12.1, with the addition of the following:

M = F⁻ concentration from calibration curve, molarity.

12.2 Average DGM Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation. Same as Method 13A, Sections 12.2 to 12.4, 12.6, and 12.7, respectively.

12.3 Total Fluoride in Sample. Calculate the amount of F⁻ in the sample using Equation 13B-1:

$$F_t = \frac{KV_t V_d M}{A_t}$$
 Eq. 13B-1

Where:

K = 19 [(mg-l)/(mole-ml)] (metric units)
= 0.292 [(gr-l)/(mole-ml)] (English units)

13.0 Method Performance

The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F⁻/m³.

13.1 Precision. The intra-laboratory and inter-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F⁻/m³ with 60 degrees of freedom and 0.056 mg F⁻/m³ with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0.02 to 2,000 µg F⁻/ml; however, measurements of less than 0.1 µg F⁻/ml require extra care.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

16.1 Compliance with ASTM D 3270-73T, 91, 95 "Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)" is an acceptable alternative for the distillation and analysis requirements specified in Sections 11.1 and 11.2 when applied to suitable aliquots of Containers 1 and 2 samples.

17.0 References

Same as Method 13A, Section 16.0, References 1 and 2, with the following addition:

1. MacLeod, Kathryn E., and Howard L. Crist. Comparison of the SPADNS-Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. *Analytical Chemistry*. 45:1272-1273. 1973.

18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

Method 14—Determination of Fluoride Emissions From Potroom Roof Monitors for Primary Aluminum Plants

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 13A, and Method 13B.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine	7782-41-4	Not determined.

1.2 Applicability. This method is applicable for the determination of fluoride emissions from roof monitors at primary aluminum reduction plant potroom groups.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Gaseous and particulate fluoride roof monitor emissions are drawn into a permanent sampling manifold through several large nozzles. The sample is transported from the sampling manifold to ground level through a duct. The fluoride content of the gas in the duct is determined using either Method 13A or Method 13B. Effluent velocity and volumetric flow rate are determined

using anemometers located in the roof monitor.

3.0 Definitions

Potroom means a building unit which houses a group of electrolytic cells in which aluminum is produced.

Potroom group means an uncontrolled potroom, a potroom which is controlled individually, or a group of potrooms or potroom segments ducted to a common control system.

Roof monitor means that portion of the roof of a potroom where gases not captured at the cell exit from the potroom.

4.0 Interferences

Same as Section 4.0 of either Method 13A or Method 13B, with the addition of the following:

4.1 Magnetic Field Effects.

Anemometer readings can be affected by potroom magnetic field effects. Section 6.1 provides for minimization of this interference through proper shielding or encasement of anemometer components.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Section 5.2 of either Method 13A or Method 13B.

6.0 Equipment and Supplies

Same as Section 6.0 of either Method 13A or Method 13B, as applicable, with the addition of the following:

6.1 Velocity Measurement

Apparatus.

6.1.1 Anemometer Specifications. Propeller anemometers, or equivalent. Each anemometer shall meet the following specifications:

6.1.1.1 Its propeller shall be made of polystyrene, or similar material of uniform density. To ensure uniformity of performance among propellers, it is desirable that all propellers be made from the same mold.

6.1.1.2 The propeller shall be properly balanced, to optimize performance.

6.1.1.3 When the anemometer is mounted horizontally, its threshold velocity shall not exceed 15 m/min (50 ft/min).

6.1.1.4 The measurement range of the anemometer shall extend to at least 600 m/min (2,000 ft/min).

6.1.1.5 The anemometer shall be able to withstand prolonged exposure to dusty and corrosive environments; one way of achieving this is to purge the bearings of the anemometer continuously with filtered air during operation.

6.1.1.6 All anemometer components shall be properly shielded or encased, such that the performance of the anemometer is uninfluenced by potroom magnetic field effects.

6.1.1.7 A known relationship shall exist between the electrical output signal from the anemometer generator and the propeller shaft rpm (see Section 10.2.1). Anemometers having other types of output signals (e.g., optical) may be used, subject to the approval of the Administrator. If other types of anemometers are used, there must be a known relationship between output signal and shaft rpm (see Section 10.2.2).

6.1.1.8 Each anemometer shall be equipped with a suitable readout system (see Section 6.1.3).

6.1.2 Anemometer Installation Requirements.

6.1.2.1 Single, Isolated Potroom. If the affected facility consists of a single, isolated potroom (or potroom segment), install at least one anemometer for every 85 m (280 ft) of roof monitor length. If the length of the roof monitor divided by 85 m (280 ft) is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. For monitors that are less than 130 m (430 ft) in length, use at least two anemometers. Divide the monitor cross-section into as many equal areas as anemometers, and locate an anemometer at the centroid of each equal area. See exception in Section 6.1.2.3.

6.1.2.2 Two or More Potrooms. If the affected facility consists of two or more potrooms (or potroom segments) ducted to a common control device, install anemometers in each potroom (or segment) that contains a sampling manifold. Install at least one anemometer for every 85 m (280 ft) of roof monitor length of the potroom (or segment). If the potroom (or segment) length divided by 85 m (280 ft) is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. If the potroom (or segment) length is less than 130 m (430 ft), use at least two anemometers. Divide the potroom (or segment) monitor cross-section into as many equal areas as anemometers, and locate an anemometer at the centroid of each equal area. See exception in Section 6.1.2.3.

6.1.2.3 Placement of Anemometer at the Center of Manifold. At least one anemometer shall be installed in the immediate vicinity (i.e., within 10 m (33 ft)) of the center of the manifold (see Section 6.2.1). For its placement in relation to the width of the monitor, there are two alternatives. The first is to make a velocity traverse of the width of the roof monitor where an anemometer is to be placed and install the anemometer at a point of average velocity along this traverse. The traverse

may be made with any suitable low velocity measuring device, and shall be made during normal process operating conditions. The second alternative is to install the anemometer half-way across the width of the roof monitor. In this latter case, the velocity traverse need not be conducted.

6.1.3 Recorders. Recorders that are equipped with suitable auxiliary equipment (e.g., transducers) for converting the output signal from each anemometer to a continuous recording of air flow velocity or to an integrated measure of volumetric flowrate shall be used. A suitable recorder is one that allows the output signal from the propeller anemometer to be read to within 1 percent when the velocity is between 100 and 120 m/min (330 and 390 ft/min). For the purpose of recording velocity, "continuous" shall mean one readout per 15-minute or shorter time interval. A constant amount of time shall elapse between readings. Volumetric flow rate may be determined by an electrical count of anemometer revolutions. The recorders or counters shall permit identification of the velocities or flowrates measured by each individual anemometer.

6.1.4 Pitot Tube. Standard-type pitot tube, as described in Section 6.7 of Method 2, and having a coefficient of 0.99 ± 0.01 .

6.1.5 Pitot Tube (Optional). Isolated, Type S pitot, as described in Section 6.1 of Method 2, and having a known coefficient, determined as outlined in Section 4.1 of Method 2.

6.1.6 Differential Pressure Gauge. Inclined manometer, or equivalent, as described in Section 6.1.2 of Method 2.

6.2 Roof Monitor Air Sampling System.

6.2.1 Manifold System and Ductwork. A minimum of one manifold system shall be installed for each potroom group. The manifold system and ductwork shall meet the following specifications:

6.2.1.1 The manifold system and connecting duct shall be permanently installed to draw an air sample from the roof monitor to ground level. A typical installation of a duct for drawing a sample from a roof monitor to ground level is shown in Figure 14-1 in Section 17.0. A plan of a manifold system that is located in a roof monitor is shown in Figure 14-2. These drawings represent a typical installation for a generalized roof monitor. The dimensions on these figures may be altered slightly to make the manifold system fit into a particular roof monitor, but the general configuration shall be followed.

6.2.1.2 There shall be eight nozzles, each having a diameter of 0.40 to 0.50 m.

6.2.1.3 The length of the manifold system from the first nozzle to the eighth shall be 35 m (115 ft) or eight percent of the length of the potroom (or potroom segment) roof monitor, whichever is greater. Deviation from this requirement is subject to the approval of the Administrator.

6.2.1.4 The duct leading from the roof monitor manifold system shall be round with a diameter of 0.30 to 0.40 m (1.0 to 1.3 ft). All connections in the ductwork shall be leak-free.

6.2.1.5 As shown in Figure 14–2, each of the sample legs of the manifold shall have a device, such as a blast gate or valve, to enable adjustment of the flow into each sample nozzle.

6.2.1.6 The manifold system shall be located in the immediate vicinity of one of the propeller anemometers (see Section 8.1.1.4) and as close as possible to the midsection of the potroom (or potroom segment). Avoid locating the manifold system near the end of a potroom or in a section where the aluminum reduction pot arrangement is not typical of the rest of the potroom (or potroom segment). The sample nozzles shall be centered in the throat of the roof monitor (see Figure 14–1).

6.2.1.7 All sample-exposed surfaces within the nozzles, manifold, and sample duct shall be constructed with 316 stainless steel. Alternatively, aluminum may be used if a new ductwork is conditioned with fluoride-laden roof monitor air for a period of six weeks before initial testing. Other materials of construction may be used if it is demonstrated through comparative testing, to the satisfaction of the Administrator, that there is no loss of fluorides in the system.

6.2.1.8 Two sample ports shall be located in a vertical section of the duct between the roof monitor and the exhaust fan (see Section 6.2.2). The sample ports shall be at least 10 duct diameters downstream and three diameters upstream from any flow disturbance such as a bend or contraction. The two sample ports shall be situated 90° apart. One of the sample ports shall be situated so that the duct can be traversed in the plane of the nearest upstream duct bend.

6.2.2 Exhaust Fan. An industrial fan or blower shall be attached to the sample duct at ground level (see Figure 14–1). This exhaust fan shall have a capacity such that a large enough volume of air can be pulled through the ductwork to maintain an isokinetic sampling rate in all the sample nozzles for all flow rates normally encountered

in the roof monitor. The exhaust fan volumetric flow rate shall be adjustable so that the roof monitor gases can be drawn isokinetically into the sample nozzles. This control of flow may be achieved by a damper on the inlet to the exhaust fan or by any other workable method.

6.3 Temperature Measurement Apparatus. To monitor and record the temperature of the roof monitor effluent gas, and consisting of the following:

6.3.1 Temperature Sensor. A temperature sensor shall be installed in the roof monitor near the sample duct. The temperature sensor shall conform to the specifications outlined in Method 2, Section 6.3.

6.3.2 Signal Transducer. Transducer, to change the temperature sensor voltage output to a temperature readout.

6.3.3 Thermocouple Wire. To reach from roof monitor to signal transducer and recorder.

6.3.4 Recorder. Suitable recorder to monitor the output from the thermocouple signal transducer.

7.0 Reagents and Standards

Same as Section 7.0 of either Method 13A or Method 13B, as applicable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Roof Monitor Velocity Determination.

8.1.1 Velocity Estimate(s) for Setting Isokinetic Flow. To assist in setting isokinetic flow in the manifold sample nozzles, the anticipated average velocity in the section of the roof monitor containing the sampling manifold shall be estimated before each test run. Any convenient means to make this estimate may be used (e.g., the velocity indicated by the anemometer in the section of the roof monitor containing the sampling manifold may be continuously monitored during the 24-hour period before the test run). If there is question as to whether a single estimate of average velocity is adequate for an entire test run (e.g., if velocities are anticipated to be significantly different during different potroom operations), the test run may be divided into two or more “sub-runs,” and a different estimated average velocity may be used for each sub-run (see Section 8.4.2).

8.1.2 Velocity Determination During a Test Run. During the actual test run, record the velocity or volumetric flowrate readings of each propeller anemometer in the roof monitor. Readings shall be taken from each anemometer at equal time intervals of 15 minutes or less (or continuously).

8.2 Temperature Recording. Record the temperature of the roof monitor

effluent gases at least once every 2 hours during the test run.

8.3 Pretest Ductwork Conditioning. During the 24-hour period immediately preceding the test run, turn on the exhaust fan, and draw roof monitor air through the manifold system and ductwork. Adjust the fan to draw a volumetric flow through the duct such that the velocity of gas entering the manifold nozzles approximates the average velocity of the air exiting the roof monitor in the vicinity of the sampling manifold.

8.4 Manifold Isokinetic Sample Rate Adjustment(s).

8.4.1 Initial Adjustment. Before the test run (or first sub-run, if applicable; see Sections 8.1.1 and 8.4.2), adjust the fan such that air enters the manifold sample nozzles at a velocity equal to the appropriate estimated average velocity determined under Section 8.1.1. Use Equation 14–1 (Section 12.2.2) to determine the correct stream velocity needed in the duct at the sampling location, in order for sample gas to be drawn isokinetically into the manifold nozzles. Next, verify that the correct stream velocity has been achieved, by performing a pitot tube traverse of the sample duct (using either a standard or Type S pitot tube); use the procedure outlined in Method 2.

8.4.2 Adjustments During Run. If the test run is divided into two or more “sub-runs” (see Section 8.1.1), additional isokinetic rate adjustment(s) may become necessary during the run. Any such adjustment shall be made just before the start of a sub-run, using the procedure outlined in Section 8.4.1 above.

Note: Isokinetic rate adjustments are not permissible during a sub-run.

8.5 Pretest Preparation, Preliminary Determinations, Preparation of Sampling Train, Leak-Check Procedures, Sampling Train Operation, and Sample Recovery. Same as Method 13A, Sections 8.1 through 8.6, with the exception of the following:

8.5.1 A single train shall be used for the entire sampling run. Alternatively, if two or more sub-runs are performed, a separate train may be used for each sub-run; note, however, that if this option is chosen, the area of the sampling nozzle shall be the same (± 2 percent) for each train. If the test run is divided into sub-runs, a complete traverse of the duct shall be performed during each sub-run.

8.5.2 Time Per Run. Each test run shall last 8 hours or more; if more than one run is to be performed, all runs shall be of approximately the same (± 10 percent) length. If questions exist as to the representativeness of an 8-hour test,

a longer period should be selected. Conduct each run during a period when all normal operations are performed underneath the sampling manifold. For most recently-constructed plants, 24 hours are required for all potroom

operations and events to occur in the area beneath the sampling manifold. During the test period, all pots in the potroom group shall be operated such that emissions are representative of

normal operating conditions in the potroom group.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
8.0, 10.0	Sampling equipment leak-check and calibration	Ensure accurate measurement of gas flow rate in duct and of sample volume.
10.3, 10.4	Initial and periodic performance checks of roof monitor effluent gas characterization apparatus.	Ensure accurate and precise measurement of roof monitor effluent gas temperature and flow rate.
11.0	Interference/recovery efficiency check during distillation.	Minimize negative effects of used acid.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 Calibration and Standardization

Same as Section 10.0 of either Method 13A or Method 13B, as applicable, with the addition of the following:

10.1 Manifold Intake Nozzles. The manifold intake nozzles shall be calibrated when the manifold system is installed or, alternatively, the manifold may be preassembled and the nozzles calibrated on the ground prior to installation. The following procedures shall be observed:

10.1.1 Adjust the exhaust fan to draw a volumetric flow rate (refer to Equation 14-1) such that the entrance velocity into each manifold nozzle approximates the average effluent velocity in the roof monitor.

10.1.2 Measure the velocity of the air entering each nozzle by inserting a standard pitot tube into a 2.5 cm or less diameter hole (see Figure 14-2) located in the manifold between each blast gate (or valve) and nozzle. Note that a standard pitot tube is used, rather than a type S, to eliminate possible velocity measurement errors due to cross-section blockage in the small (0.13 m diameter) manifold leg ducts. The pitot tube tip shall be positioned at the center of each manifold leg duct. Take care to ensure that there is no leakage around the pitot tube, which could affect the indicated velocity in the manifold leg.

10.1.3 If the velocity of air being drawn into each nozzle is not the same, open or close each blast gate (or valve) until the velocity in each nozzle is the same. Fasten each blast gate (or valve) so that it will remain in position, and close the pitot port holes.

10.2 Initial Calibration of Propeller Anemometers.

10.2.1 Anemometers that meet the specifications outlined in Section 6.1.1 need not be calibrated, provided that a reference performance curve relating anemometer signal output to air velocity (covering the velocity range of interest)

is available from the manufacturer. If a reference performance curve is not available from the manufacturer, such a curve shall be generated.

For the purpose of this method, a "reference" performance curve is defined as one that has been derived from primary standard calibration data, with the anemometer mounted vertically. "Primary standard" data are obtainable by: (a) direct calibration of one or more of the anemometers by the National Institute of Standards and Technology (NIST); (b) NIST-traceable calibration; or (c) Calibration by direct measurement of fundamental parameters such as length and time (e.g., by moving the anemometers through still air at measured rates of speed, and recording the output signals).

10.2.2 Anemometers having output signals other than electrical (e.g., optical) may be used, subject to the approval of the Administrator. If other types of anemometers are used, a reference performance curve shall be generated, using procedures subject to the approval of the Administrator.

10.2.3 The reference performance curve shall be derived from at least the following three points: 60 ± 15 , 900 ± 100 , and 1800 ± 100 rpm.

10.3 Initial Performance Checks. Conduct these checks within 60 days before the first performance test.

10.3.1 Anemometers. A performance-check shall be conducted as outlined in Sections 10.3.1.1 through 10.3.1.3. Alternatively, any other suitable method that takes into account the signal output, propeller condition, and threshold velocity of the anemometer may be used, subject to the approval of the Administrator.

10.3.1.1 Check the signal output of the anemometer by using an accurate rpm generator (see Figure 14-3) or synchronous motors to spin the propeller shaft at each of the three rpm settings described in Section 10.2.3, and measuring the output signal at each setting. If, at each setting, the output

signal is within 5 percent of the manufacturer's value, the anemometer can be used. If the anemometer performance is unsatisfactory, the anemometer shall either be replaced or repaired.

10.3.1.2 Check the propeller condition, by visually inspecting the propeller, making note of any significant damage or warpage; damaged or deformed propellers shall be replaced.

10.3.1.3 Check the anemometer threshold velocity as follows: With the anemometer mounted as shown in Figure 14-4(A), fasten a known weight (a straight-pin will suffice) to the anemometer propeller at a fixed distance from the center of the propeller shaft. This will generate a known torque; for example, a 0.1-g weight, placed 10 cm from the center of the shaft, will generate a torque of 1.0 g-cm. If the known torque causes the propeller to rotate downward, approximately 90° [see Figure 14-4(B)], then the known torque is greater than or equal to the starting torque; if the propeller fails to rotate approximately 90°, the known torque is less than the starting torque. By trying different combinations of weight and distance, the starting torque of a particular anemometer can be satisfactorily estimated. Once an estimate of the starting torque has been obtained, the threshold velocity of the anemometer (for horizontal mounting) can be estimated from a graph such as Figure 14-5 (obtained from the manufacturer). If the horizontal threshold velocity is acceptable [<15 m/min (50 ft/min), when this technique is used], the anemometer can be used. If the threshold velocity of an anemometer is found to be unacceptably high, the anemometer shall either be replaced or repaired.

10.3.2 Recorders and Counters. Check the calibration of each recorder and counter (see Section 6.1.2) at a minimum of three points, approximately spanning the expected range of velocities. Use the calibration

procedures recommended by the manufacturer, or other suitable procedures (subject to the approval of the Administrator). If a recorder or counter is found to be out of calibration by an average amount greater than 5 percent for the three calibration points, replace or repair the system; otherwise, the system can be used.

10.3.3 Temperature Measurement Apparatus. Check the calibration of the Temperature Measurement Apparatus, using the procedures outlined in Section 10.3 of Method 2, at temperatures of 0, 100, and 150 °C (32, 212, and 302 °F). If the calibration is off by more than 5 °C (9 °F) at any of the temperatures, repair or replace the apparatus; otherwise, the apparatus can be used.

10.4 Periodic Performance Checks. Repeat the procedures outlined in Section 10.3 no more than 12 months after the initial performance checks. If the above systems pass the performance checks (*i.e.*, if no repair or replacement of any component is necessary), continue with the performance checks on a 12-month interval basis. However, if any of the above systems fail the performance checks, repair or replace the system(s) that failed, and conduct the periodic performance checks on a 3-month interval basis, until sufficient information (to the satisfaction of the Administrator) is obtained to establish a modified performance check schedule and calculation procedure.

Note: If any of the above systems fails the 12-month periodic performance checks, the data for the past year need not be recalculated.

11.0 Analytical Procedures

Same as Section 11.0 of either Method 13A or Method 13B.

12.0 Data Analysis and Calculations

Same as Section 12.0 of either Method 13A or Method 13B, as applicable, with the following additions and exceptions:

12.1 Nomenclature.

A = Roof monitor open area, m² (ft²).

B_{ws} = Water vapor in the gas stream, portion by volume.

C_s = Average fluoride concentration in roof monitor air, mg F/dscm (gr/dscf).

D_d = Diameter of duct at sampling location, m (ft).

D_n = Diameter of a roof monitor manifold nozzle, m (ft).

F = Emission Rate multiplication factor, dimensionless.

F_t = Total fluoride mass collected during a particular sub-run (from Equation 13A-1 of Method 13A or Equation 13B-1 of Method 13B), mg F⁻ (gr F⁻).

M_d = Mole fraction of dry gas, dimensionless.

P_{rm} = Pressure in the roof monitor; equal to barometric pressure for this application.

Q_{sd} = Average volumetric flow from roof monitor at standard conditions on a dry basis, m³/min.

T_{rm} = Average roof monitor temperature (from Section 8.2), °C (°F).

V_d = Desired velocity in duct at sampling location, m/sec.

V_m = Anticipated average velocity (from Section 8.1.1) in sampling duct, m/sec.

V_{mt} = Arithmetic mean roof monitor effluent gas velocity, m/sec.

V_s = Actual average velocity in the sampling duct (from Equation 2-9 of Method 2 and data obtained from Method 13A or 13B), m/sec.

12.2 Isokinetic Sampling Check.

12.2.1 Calculate the arithmetic mean of the roof monitor effluent gas velocity readings (v_m) as measured by the anemometer in the section of the roof monitor containing the sampling manifold. If two or more sub-runs have been performed, the average velocity for each sub-run may be calculated separately.

12.2.2 Calculate the expected average velocity (v_d) in the duct, corresponding to each value of v_m obtained under Section 12.2.1, using Equation 14-1.

$$V_d = \frac{8D_n^2 V_m}{60D_d^2} \quad \text{Eq. 14-1}$$

Where:

8 = number of required manifold nozzles.

60 = sec/min.

12.2.3 Calculate the actual average velocity (v_s) in the sampling duct for each run or sub-run according to Equation 2-9 of Method 2, using data obtained during sampling (Section 8.0 of Method 13A).

12.2.4 Express each v_s value from Section 12.2.3 as a percentage of the corresponding v_d value from Section 12.2.2.

12.2.4.1 If v_s is less than or equal to 120 percent of v_d, the results are acceptable (note that in cases where the above calculations have been performed for each sub-run, the results are acceptable if the average percentage for all sub-runs is less than or equal to 120 percent).

12.2.4.2 If v_s is more than 120 percent of v_d, multiply the reported emission rate by the following factor:

$$F = 1 + \frac{100 V_s}{V_d} - 120 \quad \text{Eq. 14-2}$$

12.3 Average Velocity of Roof Monitor Effluent Gas. Calculate the arithmetic mean roof monitor effluent gas velocity (v_m) using all the velocity or volumetric flow readings from Section 8.1.2.

12.4 Average Temperature of Roof Monitor Effluent Gas. Calculate the arithmetic mean roof monitor effluent gas temperature (T_m) using all the temperature readings recorded in Section 8.2.

12.5 Concentration of Fluorides in Roof Monitor Effluent Gas.

12.5.1 If a single sampling train was used throughout the run, calculate the average fluoride concentration for the roof monitor using Equation 13A-2 of Method 13A.

12.5.2 If two or more sampling trains were used (*i.e.*, one per sub-run), calculate the average fluoride concentration for the run using Equation 14-3:

$$C_s = \frac{\sum_{i=1}^n (F_t)_i}{\sum_{i=1}^n (V_{m(st)})_i} \quad \text{Eq. 14-3}$$

Where:

n = Total number of sub-runs.

12.6 Mole Fraction of Dry Gas.

$$M_d = 1 - B_{ws} \quad \text{Eq. 14-4}$$

12.7 Average Volumetric Flow Rate of Roof Monitor Effluent Gas. Calculate the arithmetic mean volumetric flow rate of the roof monitor effluent gases using Equation 14-5.

$$Q_{sd} = \frac{K_1 V_{mt} M_d P_m A}{T_{rm}} \quad \text{Eq. 14-5}$$

Where:

K₁ = 0.3858 K/mm Hg for metric units, = 17.64 °R/in. Hg for English units.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

Same as Section 16.0 of either Method 13A or Method 13B, as applicable, with the addition of the following:

1. Shigehara, R.T. A Guideline for Evaluating Compliance Test Results (Isokinetic Sampling Rate Criterion). U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. August 1977.

BILLING CODE 6560-50-P

17.0 Tables, Diagrams, Flowcharts, and Validation Data

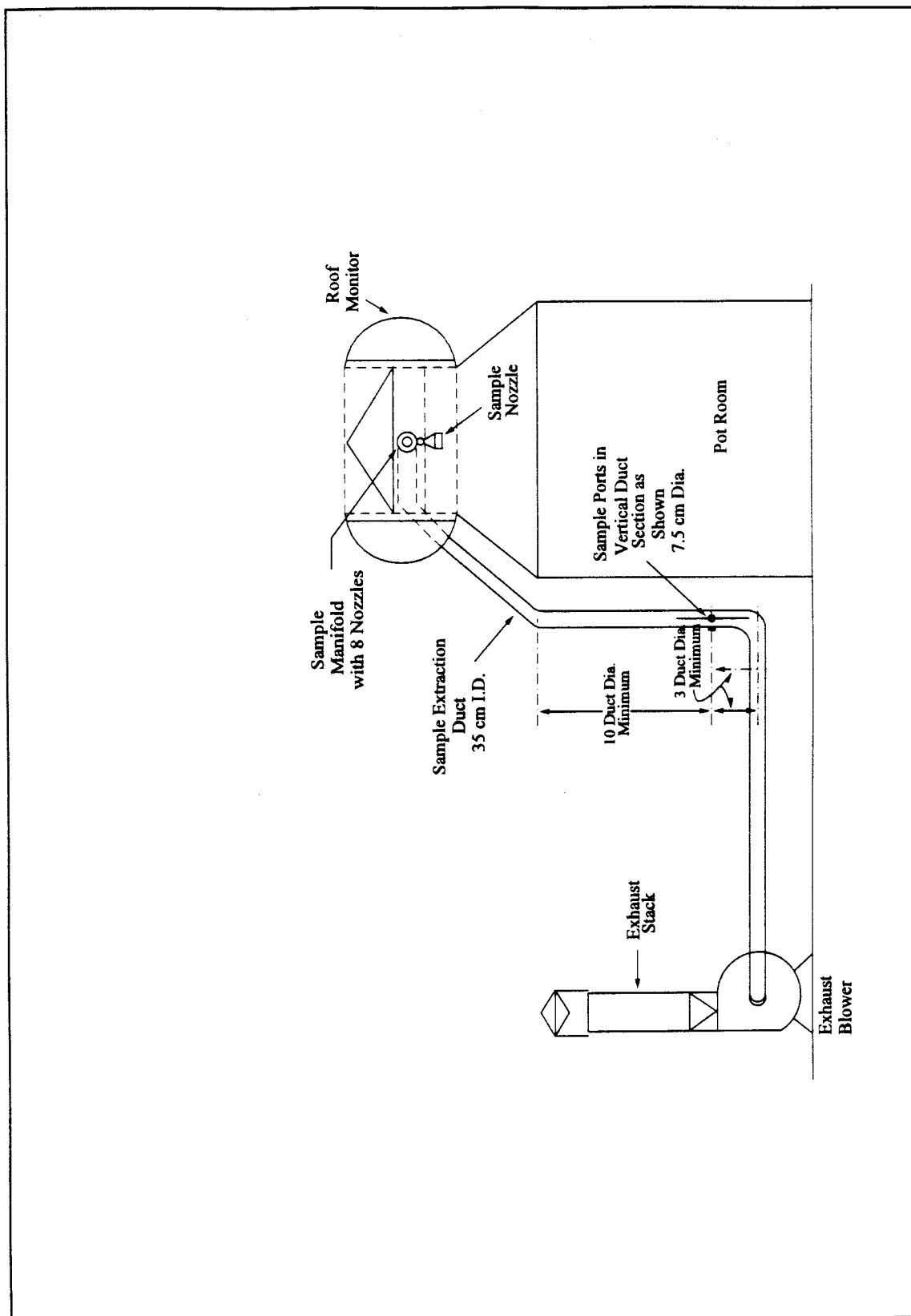


Figure 14-1. Roof Monitor Sampling System.

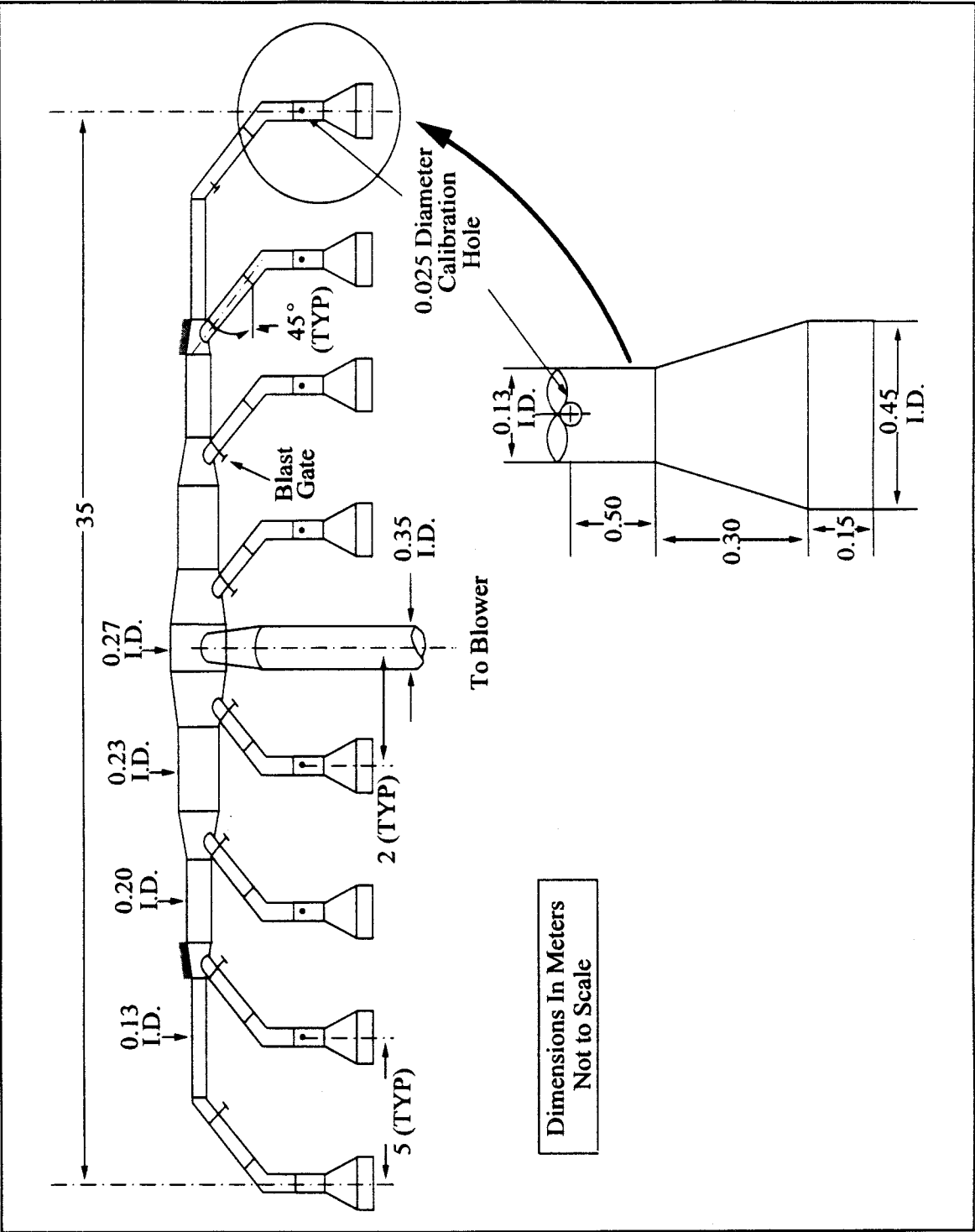


Figure 14-2. Sampling Manifold and Nozzles.

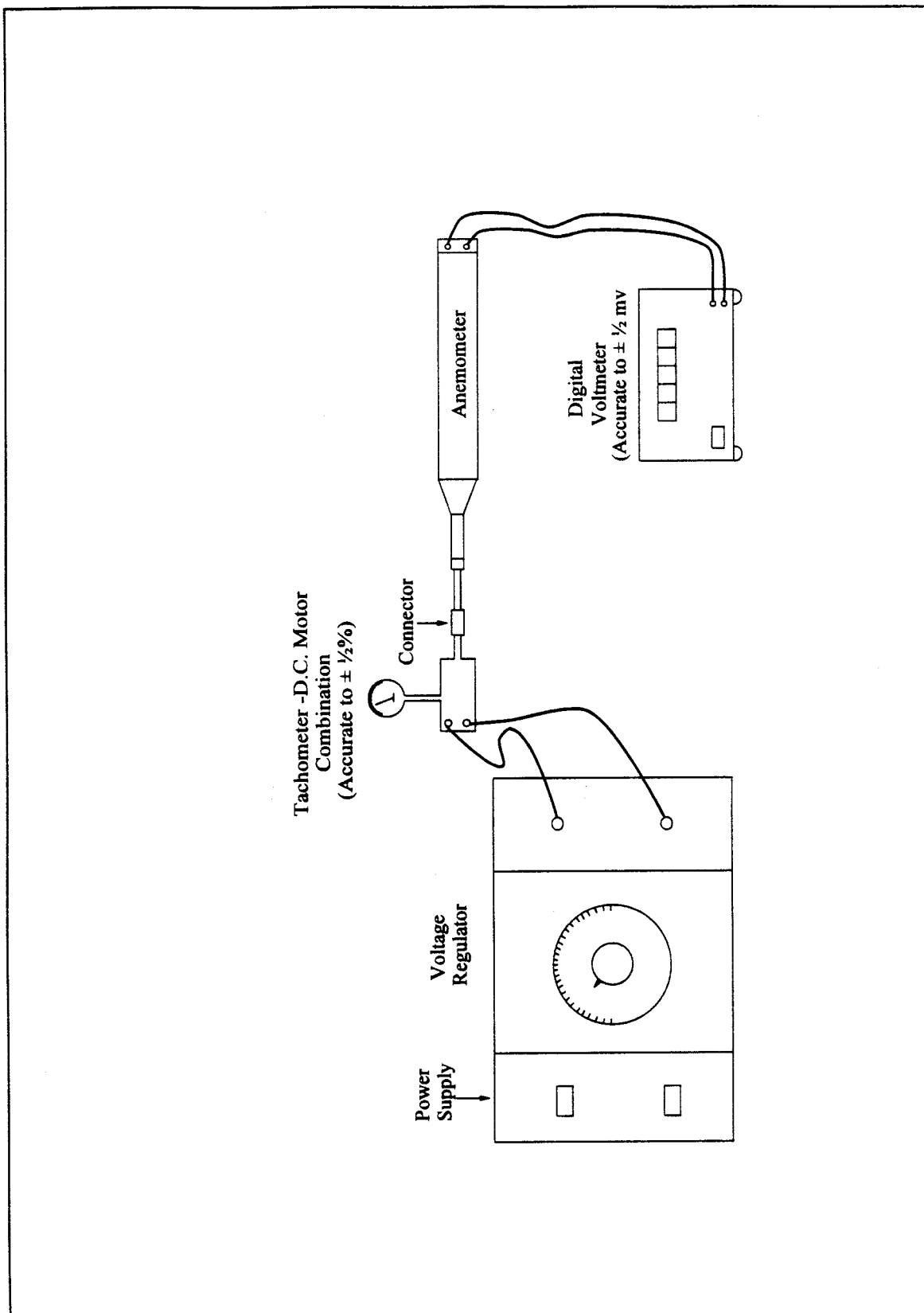


Figure 14-3. Typical RPM Generator.

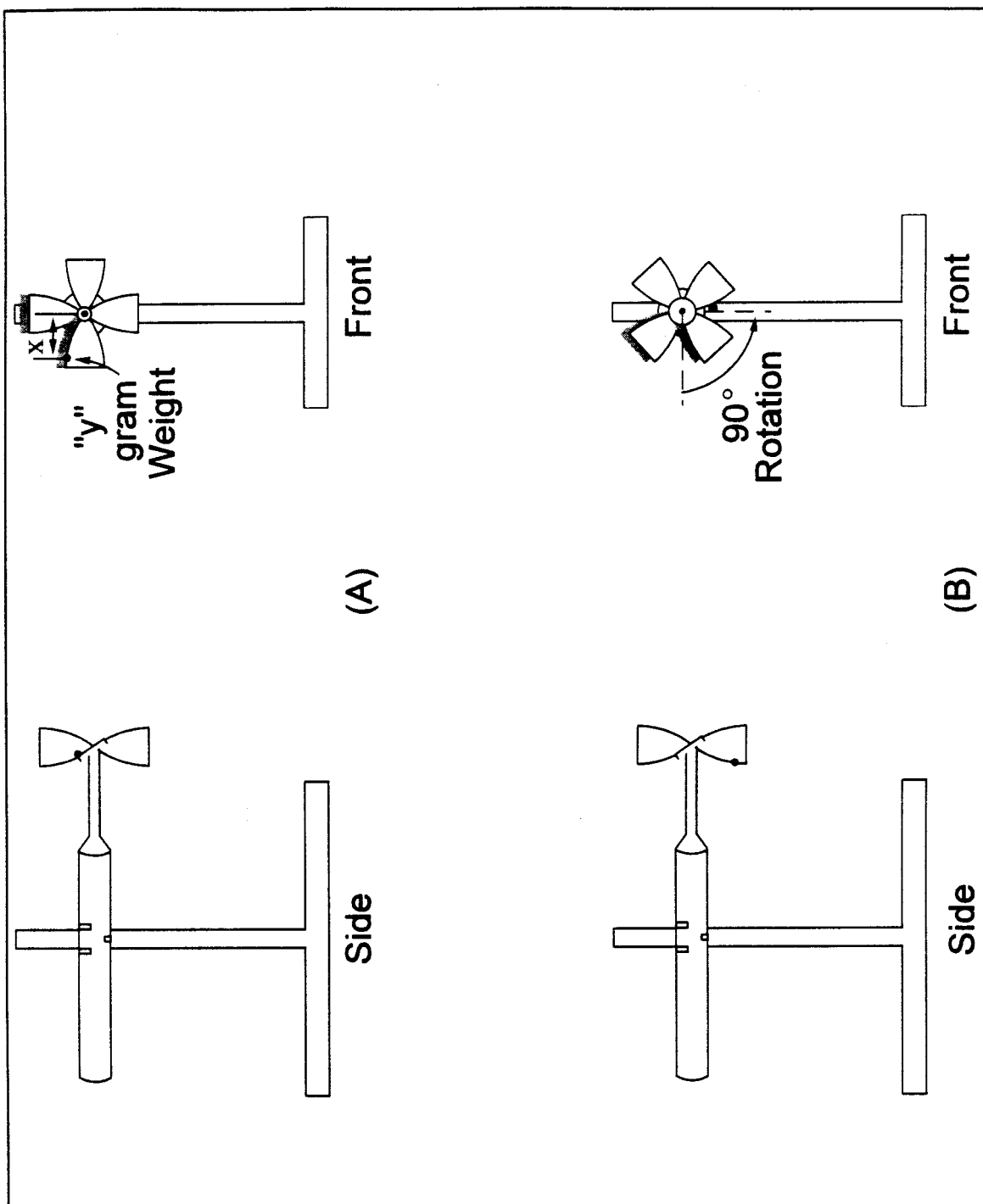


Figure 14-4. Check of Anemometer Starting Torque.

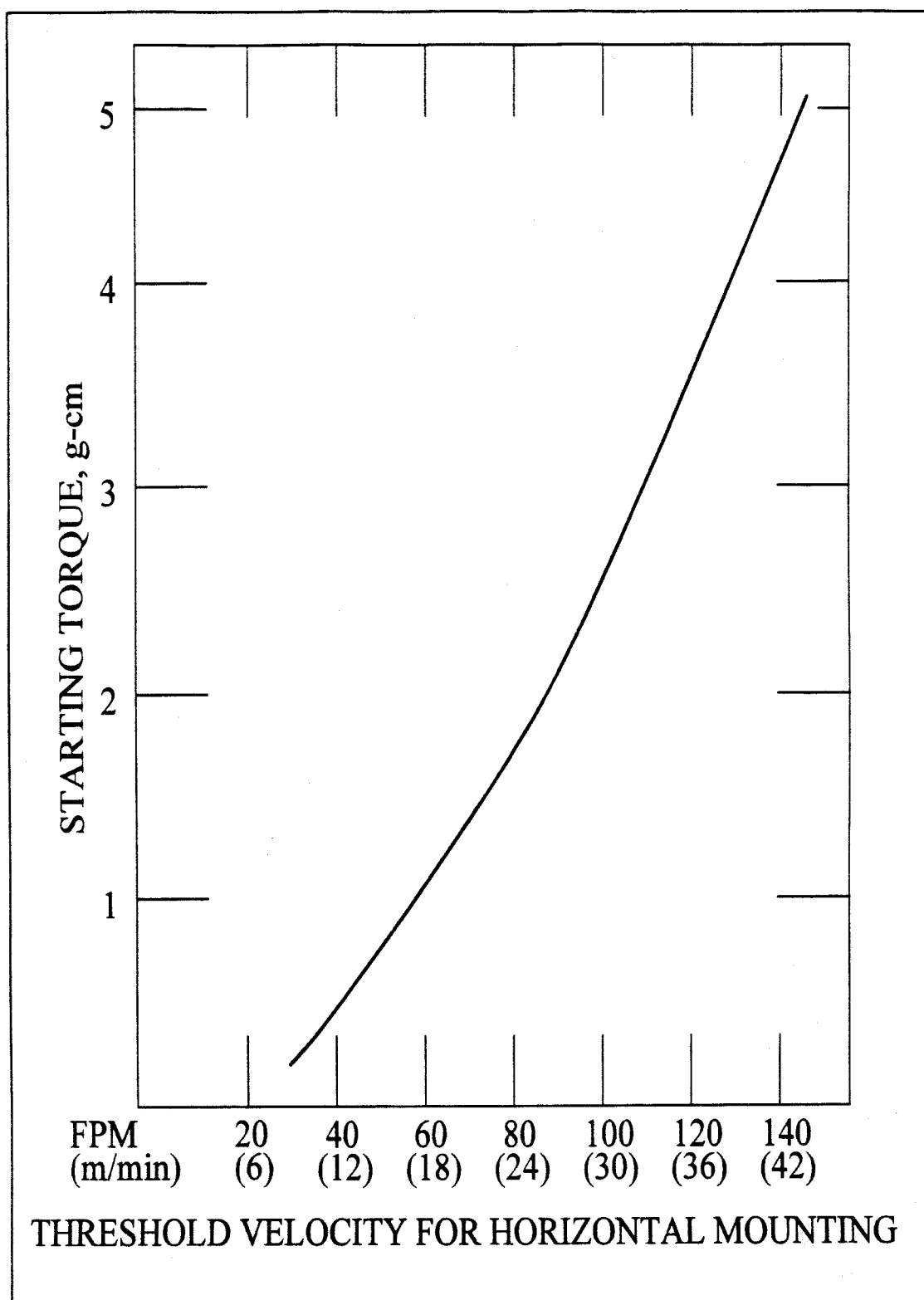


Figure 14-5. Typical Curve of Starting Torque vs. Horizontal Threshold Velocity for Propeller Anemometers.

* * * * *

Method 15—Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions From Stationary Sources

Note: This method is not inclusive with respect to specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of gas chromatography techniques.

1.0 Scope and Application**1.1 Analytes.**

Analyte	CAS No.	Sensitivity (See Sec 13.2)
Carbon disulfide [CS ₂]	75–15–0	0.5 ppmv
Carbonyl sulfide [COS]	463–58–1	0.5 ppmv
Hydrogen sulfide [H ₂ S]	7783–06–4	0.5 ppmv

1.2 Applicability.

1.2.1 This method applies to the determination of emissions of reduced sulfur compounds from tail gas control units of sulfur recovery plants, H₂S in fuel gas for fuel gas combustion devices, and where specified in other applicable subparts of the regulations.

1.2.2 The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods for determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample-line loss criteria are met.

1.3 Data Quality Objectives.

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the emission source and diluted with clean dry air (if necessary). An aliquot of the diluted sample is then analyzed for CS₂, COS, and H₂S by GC/FPD.

3.0 Definitions. [Reserved]**4.0 Interferences****4.1 Moisture Condensation.**

Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the probe, filter box, and connections, and by maintaining the SO₂ scrubber in an ice water bath. Moisture is removed in the SO₂ scrubber and heating the sample beyond this point is not necessary provided the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating

temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO₂). CO and CO₂ have substantial desensitizing effects on the FPD even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting CO and CO₂ before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO₂ in the diluent gas. The CO₂ level should be approximately 10 percent for the case with CO₂ present. The two chromatograms should show agreement within the precision limits of Section 13.3.

4.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling system can lead to blockage of the particulate filter. This problem can be minimized by observing the filter for buildup and changing as needed.

4.4 Sulfur Dioxide (SO₂). SO₂ is not a specific interferer but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO₂ scrubber described in Section 6.1.3 will effectively remove SO₂ from the sample.

4.5 Alkali Mist. Alkali mist in the emissions of some control devices may cause a rapid increase in the SO₂ scrubber pH, resulting in low sample recoveries. Replacing the SO₂ scrubber contents after each run will minimize the chances of interference in these cases.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test to establish appropriate safety and health practices and determine the applicability of regulatory limitations to performing this test.

6.0 Equipment and Supplies

6.1 Sample Collection. See Figure 15–1. The sampling train component parts are discussed in the following sections:

6.1.1 Probe. The probe shall be made of Teflon or Teflon-lined stainless steel and heated to prevent moisture condensation. It shall be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. The probe described in Section 6.1.1 of Method 16A having a nozzle directed away from the gas stream is recommended for sources having particulate or mist emissions. Where very high stack temperatures prohibit the use of Teflon probe components, glass or quartz-lined probes may serve as substitutes.

6.1.2 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO₂ Scrubber. Three 300-ml Teflon segment impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3-mm (1/8-in.) ID and should be immersed to a depth of at least 50 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C. The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO₂ scrubber shall be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior

to the SO₂ scrubber (or alternative point of moisture removal) shall be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 **Sample Line.** Teflon, no greater than 13-mm (¹/₂-in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line-loss test is acceptable.

6.1.5 **Sample Pump.** The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent.

6.2 **Analysis.** The following items are needed for sample analysis:

6.2.1 **Dilution System.** The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel. It must be capable of approximately a 9:1 dilution of the sample.

6.2.2 **Gas Chromatograph** (see Figure 15-2). The gas chromatograph must have at least the following components:

6.2.2.1 **Oven.** Capable of maintaining the separation column at the proper operating temperature ± 1 °C.

6.2.2.2 **Temperature Gauge.** To monitor column oven, detector, and exhaust temperature ± 1 °C.

6.2.2.3 **Flow System.** Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 **Flame Photometric Detector.**

6.2.2.4.1 **Electrometer.** Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

6.2.2.4.2 **Power Supply.** Capable of delivering up to 750 volts.

6.2.2.5 **Recorder.** Compatible with the output voltage range of the electrometer.

6.2.2.6 **Rotary Gas Valves.** Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes shall be chosen to provide the needed analytical range. Teflon tubing and fittings shall be used throughout to present an inert surface for sample gas. The GC shall be calibrated with the sample loop used for sample analysis.

6.2.2.7 **GC Columns.** The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H₂S, COS, and CS₂. To demonstrate that adequate resolution has been achieved, a chromatogram of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard must be submitted. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero (± 5 percent) in the interval between peaks. Systems not meeting this criteria may be considered

alternate methods subject to the approval of the Administrator.

6.3 **Calibration System** (See Figure 15-3). The calibration system must contain the following components:

6.3.1 **Flow System.** To measure air flow over permeation tubes within 2 percent. Each flowmeter shall be calibrated after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by more than 5 percent, the completed test shall be discarded.

Alternatively, use the flow data that will yield the lowest flow measurement. Calibration with a wet-test meter before a test is optional. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.2 **Constant Temperature Bath.** Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C.

6.3.3 **Temperature Sensor.** Thermometer or equivalent to monitor bath temperature within 0.1 °C.

7.0 **Reagents and Standards**

7.1 **Fuel.** Hydrogen gas (H₂).

Prepurified grade or better.

7.2 **Combustion Gas.** Oxygen (O₂) or air, research purity or better.

7.3 **Carrier Gas.** Purified grade or better.

7.4 **Diluent.** Air containing less than 0.5 ppmv total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 **Calibration Gases.**

7.5.1 **Permeation Devices.** One each of H₂S, COS, and CS₂, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 **Cylinder Gases.** Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 **Citrate Buffer.** Dissolve 300 g of potassium citrate and 41 g of anhydrous citric acid in 1 liter of water. Alternatively, 284 g of sodium citrate may be substituted for the potassium citrate. Adjust the pH to between 5.4

and 5.6 with potassium citrate or citric acid, as required.

8.0 **Sample Collection, Preservation, Transport, and Storage**

8.1 **Pretest Procedures.** After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated. These procedures are not required, but would be helpful in preventing any problem which might occur later to invalidate the entire test.

8.1.1 **Leak-Check.** Appropriate leak-check procedures should be employed to verify the integrity of all components, sample lines, and connections. The following procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak. As an alternative to the initial leak-test, the sample line loss test described in Section 8.3.1 may be performed to verify the integrity of components.

8.1.2 **System Performance.** Since the complete system is calibrated at the beginning and end of each day of testing, the precise calibration of each component is not critical. However, these components should be verified to operate properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations, respectively, and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8.2 **Sample Collection and Analysis**

8.2.1 After performing the calibration procedures outlined in Section 10.0, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is the one determined in Section 10.4. Condition the entire system with sample for a minimum of 15 minutes before beginning the analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis.

Determine the concentration of each reduced sulfur compound directly from the calibration curves or from the equation for the least-squares line.

8.2.2 If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe or filter is clogged with particulate matter. If either is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning or replacing the probe and filter. After each run, the probe and filter shall be inspected and, if necessary, replaced.

8.2.3 A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

8.3 Post-Test Procedures.

8.3.1 Sample Line Loss. A known concentration of H₂S at the level of the

applicable standard, ± 20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the same manner as the emission samples. The resulting measured concentration is compared to the known value to determine the sampling system loss. For sampling losses greater than 20 percent, the previous sample run is not valid. Sampling losses of 0–20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be calibration gas as described in Section 7.5. Alternatively, cylinder gas containing H₂S mixed in nitrogen and verified according to Section 7.1.4 of Method 16A may be

used. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

8.3.2 Determination of Calibration Drift. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 10.0. Only H₂S (or other permeant) need be used to recalibrate the GC/FPD analysis system and the dilution system. Compare the calibration curves obtained after the runs to the calibration curves obtained under Section 10.3. The calibration drift should not exceed the limits set forth in Section 13.4. If the drift exceeds this limit, the intervening run or runs should be considered invalid. As an option, the calibration data set which gives the highest sample values may be chosen by the tester.

9.0 Quality Control

Section	Quality control measure	Effect
8.3.1	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.3.2	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. However, the calibration drift must be determined as prescribed in Section 8.3.2 after the last run is made within the 24-hour period.)

Note: This section outlines steps to be followed for use of the GC/FPD and the dilution system. The calibration procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components, particularly the GC/FPD. The references in Section 16.0 are recommended for review for this purpose.

10.1 Calibration Gas Permeation Tube Preparation.

10.1.1 Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within 0.1 °C. Allow 24 hours for the tubes to equilibrate. Alternatively,

equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within 5 percent of their mean.

10.1.2 Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in ppmv generated by a tube containing a specific permeant can be calculated using Equation 15–1 in Section 12.2.

10.2 Calibration of Analytical System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.5 to 10 ppmv for a 1-ml sample) for each of the three major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD and monitor the responses until three consecutive injections for each concentration agree within 5 percent of their mean. Failure to attain this precision indicates a problem in the calibration or analytical system. Any such problem must be

identified and corrected before proceeding.

10.3 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppmv on log-log coordinate graph paper for each sulfur compound. Alternatively, a least-squares equation may be generated from the calibration data using concentrations versus the appropriate instrument response units.

10.4 Calibration of Dilution System. Generate a known concentration of H₂S using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system until the results of three consecutive injections for each dilution agree within 5 percent of their mean. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H₂S (developed under Section 10.3), determine the diluted calibration gas concentration in ppmv. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this section. Repeat this procedure for each

stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. These data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements are still applicable.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see Section 8.0).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C = Concentration of permeant produced, ppmv.

COS = Carbonyl sulfide concentration, ppmv.

CS₂ = Carbon disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

H₂S = Hydrogen sulfide concentration, ppmv.

K = 24.04 L/g mole. (Gas constant at 20°C and 760 mm Hg)

L = Flow rate, L/min, of air over permeant 20°C, 760 mm Hg.

M = Molecular weight of the permeant, g/g-mole.

N = Number of analyses performed.

P_r = Permeation rate of the tube, µg/min.

12.2 Permeant Concentration.

Calculate the concentration generated by a tube containing a specific permeant (see Section 10.1) using the following equation:

$$C = \frac{K P_r}{M L} \quad \text{Eq. 15-1}$$

12.3 Calculation of SO₂ Equivalent. SO₂ equivalent will be determined for each analysis made by summing the

concentrations of each reduced sulfur compound resolved during the given

analysis. The SO₂ equivalent is expressed as SO₂ in ppmv.

$$\text{SO}_2 \text{ equivalent}_i = \sum (\text{H}_2\text{S}, \text{COS}, 2\text{CS}_2) d \quad \text{Eq. 15-2}$$

12.4 Average SO₂ Equivalent. This is determined using the following equation. Systems that do not remove moisture from the sample but condition the gas to prevent condensation must correct the average SO₂ equivalent for the fraction of water vapor present. This is not done under applications where the emission standard is not specified on a dry basis.

$$\text{Avg SO}_2 \text{ equivalent} = \frac{\sum_{i=1}^n \text{SO}_2 \text{ equivalent}_i}{N} \quad \text{Eq. 15-3}$$

Where:

Avg SO₂ equivalent = Average SO₂ equivalent in ppmv, dry basis.

Average SO₂ equivalent_i = SO₂ in ppmv as determined by Equation 15-2.

13.0 Method Performance

13.1 Range. Coupled with a GC system using a 1-ml sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppmv. It may be necessary to dilute samples from sulfur recovery plants a hundredfold (99:1), resulting in an upper limit of about 1000 ppmv for each compound.

13.2 Sensitivity. The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppmv for a 1-ml sample.

13.3 Calibration Precision. A series of three consecutive injections of the

same calibration gas, at any dilution, shall produce results which do not vary by more than 5 percent from the mean of the three injections.

13.4 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any run or series of runs within a 24-hour period shall not exceed 5 percent.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References.

1. O'Keeffe, A.E., and G.C. Ortman. "Primary Standards for Trace Gas Analysis." Anal. Chem. 38,760. 1966.

2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels." Environmental Science and Technology 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA, April 6-8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." Pulp and Paper Magazine of Canada, 73,3. March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting in St. Louis, MO. June 14-19, 1970.

6. General Reference. Standard Methods of Chemical Analysis Volume III-A and III-B: Instrumental Analysis. Sixth Edition. Van Nostrand Reinhold Co.

BILLING CODE 6560-50-P

17.0 Tables, Diagrams, Flowcharts, and Validation Data

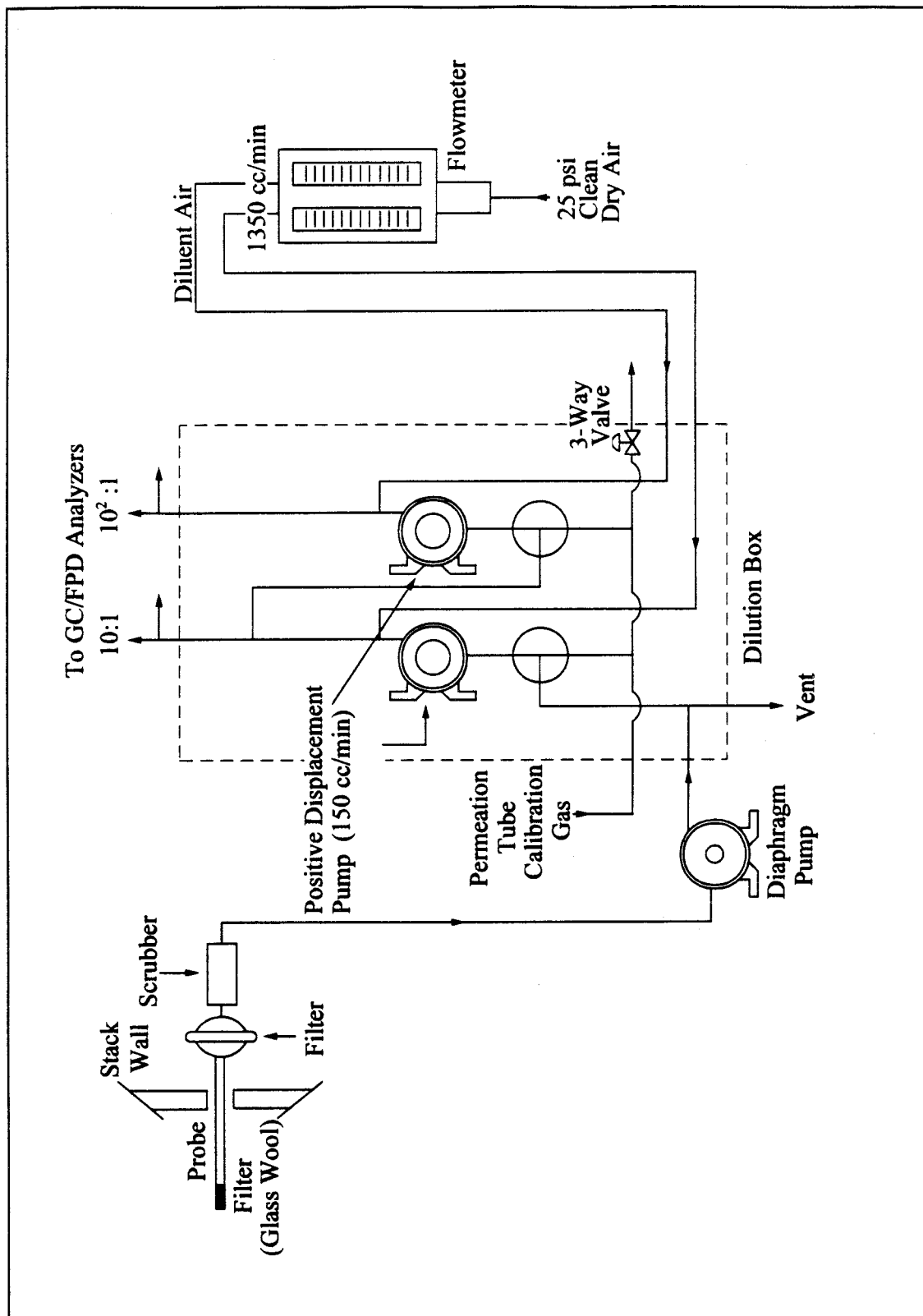


Figure 15-1. Sampling and Dilution Apparatus.

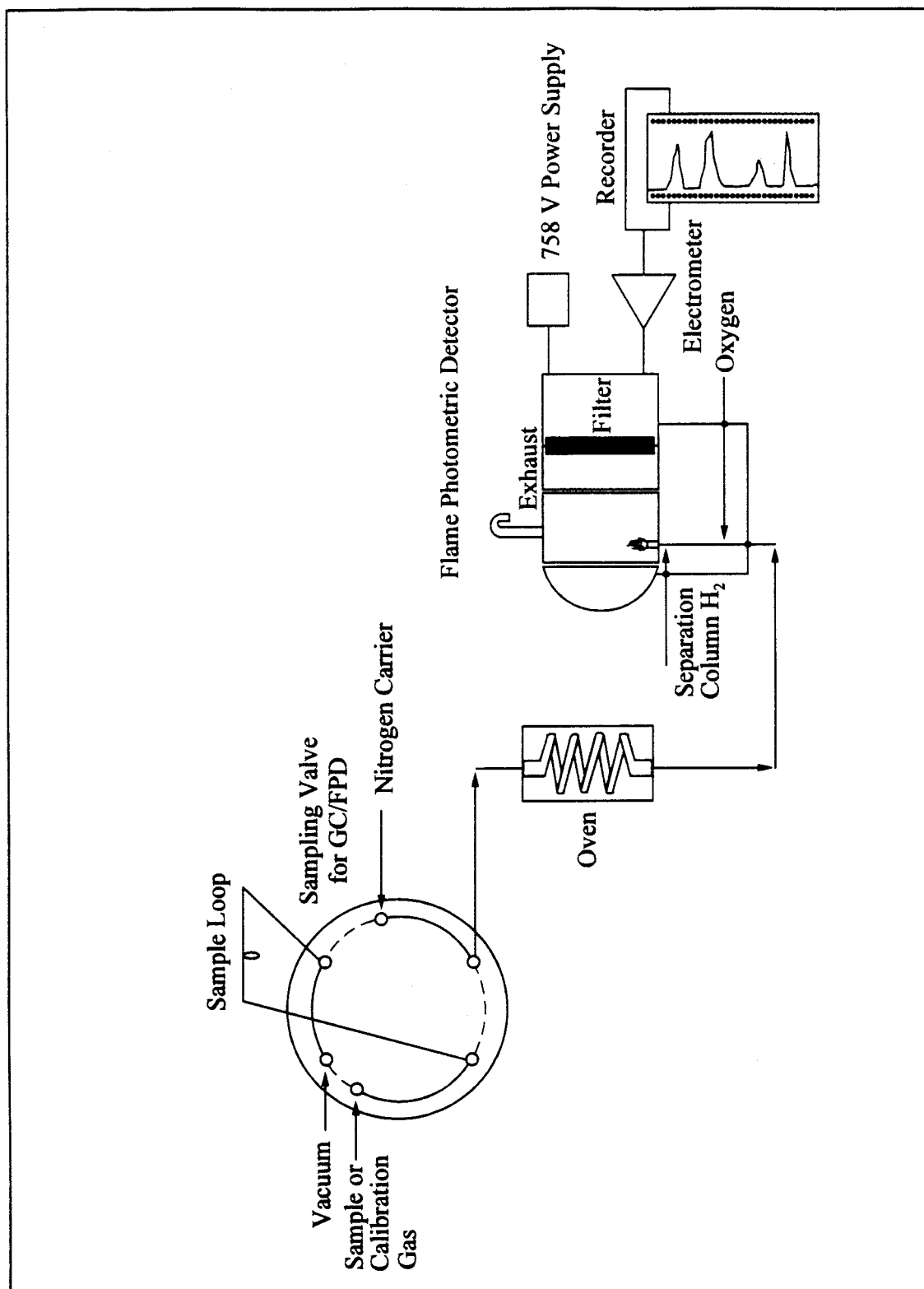


Figure 15-2. Gas Chromatographic Flame Photometric Analyzer.

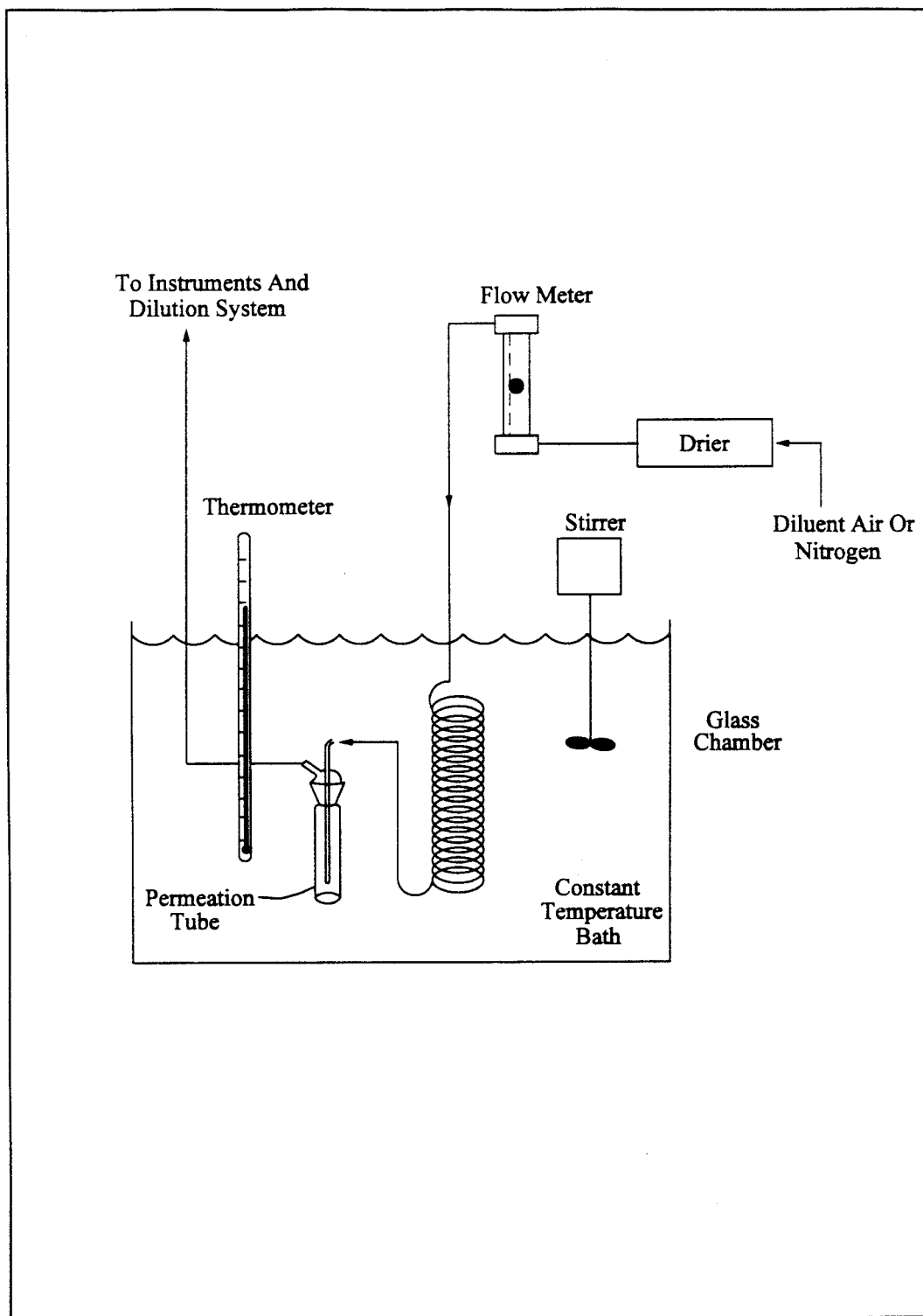


Figure 15-3. Apparatus for Field Calibration.

Method 15A—Determination of Total Reduced Sulfur Emissions From Sulfur Recovery Plants in Petroleum Refineries

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 6, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Reduced sulfur compounds	None assigned	Not determined.

1.2 Applicability. This method is applicable for the determination of emissions of reduced sulfur compounds from sulfur recovery plants where the emissions are in a reducing atmosphere, such as in Stretford units.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack, and combustion air is added to the oxygen (O_2)-deficient gas at a known rate. The reduced sulfur compounds [including carbon disulfide (CS_2), carbonyl sulfide (COS), and hydrogen sulfide (H_2S)] are thermally oxidized to sulfur dioxide (SO_2), which is then collected in hydrogen peroxide as sulfate ion and analyzed according to the Method 6 barium-thorin titration procedure.

3.0 Definitions. [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds, other than CS_2 , COS , and H_2S , that are present in the emissions will also be oxidized to SO_2 , causing a positive bias relative to emission standards that limit only the three compounds listed above. For example, thiophene has been identified in emissions from a Stretford unit and produced a positive bias of 30 percent in the Method 15A result. However, these biases may not affect the outcome of the test at units where emissions are low relative to the standard.

4.2 Calcium and aluminum have been shown to interfere in the Method 6 titration procedure. Since these metals have been identified in particulate matter emissions from Stretford units, a Teflon filter is required to minimize this interference.

4.3 Dilution of the hydrogen peroxide (H_2O_2) absorbing solution can potentially reduce collection efficiency, causing a negative bias. When used to sample emissions containing 7 percent moisture or less, the midjet impingers have sufficient volume to contain the

condensate collected during sampling. Dilution of the H_2O_2 does not affect the collection of SO_2 . At higher moisture contents, the potassium citrate-citric acid buffer system used with Method 16A should be used to collect the condensate.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide ($NaOH$). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train used in performing this method is shown in Figure 15A-1, and component parts are discussed below. Modifications to this sampling train are

acceptable provided that the system performance check is met.

6.1.1 Probe. 6.4-mm ($\frac{1}{4}$ -in.) OD Teflon tubing sequentially wrapped with heat-resistant fiber strips, a rubberized heating tape (with a plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or some other suitable temperature-measuring device shall be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent flue gas from entering between the probe and sheath. The sampling probe is depicted in Figure 15A-2.

6.1.2 Particulate Filter. A 50-mm Teflon filter holder and a 1- to 2-mm porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55345). The filter holder must be maintained in a hot box at a temperature high enough to prevent condensation.

6.1.3 Combustion Air Delivery System. As shown in the schematic diagram in Figure 15A-3. The rate meter should be selected to measure an air flow rate of 0.5 liter/min ($0.02\text{ ft}^3/\text{min}$).

6.1.4 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm ($\frac{1}{4}$ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90 degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.5 Furnace. Of sufficient size to enclose the combustion tube. The furnace must have a temperature regulator capable of maintaining the temperature at $1100 \pm 50^\circ\text{C}$ ($2,012 \pm 90^\circ\text{F}$). The furnace operating temperature must be checked with a thermocouple to ensure accuracy. Lindberg furnaces have been found to be satisfactory.

6.1.6 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as in Method 6, Sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, Section 6.1.1.2 is not required.

6.1.7 Vacuum Gauge and Rate Meter. At least 760 mm Hg (30 in. Hg) gauge and rotameter, or equivalent, capable of measuring flow rate to ± 5 percent of the selected flow rate and calibrated as in Section 10.2.

6.1.8 Volume Meter. Dry gas meter capable of measuring the sample volume under the particular sampling conditions with an accuracy of 2 percent.

6.1.9 U-tube manometer. To measure the pressure at the exit of the combustion gas dry gas meter.

6.2 Sample Recovery and Analysis. Same as Method 6, Sections 6.2 and 6.3, except a 10-ml buret with 0.05-ml graduations is required for titrant volumes of less than 10.0 ml, and the spectrophotometer is not needed.

7.0 Reagents and Standards

Note: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade shall be used.

7.1 Sample Collection. The following reagents and standards are required for sample analysis:

7.1.1 Water. Same as Method 6, Section 7.1.1.

7.1.2 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Same as Method 6, Section 7.1.3 (40 ml is needed per sample).

7.1.3 Recovery Check Gas. Carbonyl sulfide in nitrogen [100 parts per million by volume (ppmv) or greater, if necessary] in an aluminum cylinder. Concentration certified by the manufacturer with an accuracy of ± 2 percent or better, or verified by gas chromatography where the instrument is calibrated with a COS permeation tube.

7.1.4 Combustion Gas. Air, contained in a gas cylinder equipped with a two-stage regulator. The gas shall contain less than 50 ppb of reduced sulfur compounds and less than 10 ppm total hydrocarbons.

7.2 Sample Recovery and Analysis. Same as Method 6, Sections 7.2 and 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. For the Method 6 part of the train,

measure 20 ml of 3 percent H_2O_2 into the first and second midget impingers. Leave the third midget impinger empty and add silica gel to the fourth impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Place crushed ice and water around all impingers. Maintain the oxidation furnace at $1100 \pm 50^\circ\text{C}$ ($2,012 \pm 90^\circ\text{F}$) to ensure 100 percent oxidation of COS. Maintain the probe and filter temperatures at a high enough level (no visible condensation) to prevent moisture condensation and monitor the temperatures with a thermocouple.

8.2 Leak-Check Procedure. Assemble the sampling train and leak-check as described in Method 6, Section 8.2. Include the combustion air delivery system from the needle valve forward in the leak-check.

8.3 Sample Collection. Adjust the pressure on the second stage of the regulator on the combustion air cylinder to 10 psig. Adjust the combustion air flow rate to 0.5 ± 0.05 L/min (1.1 ± 0.1 ft³/hr) before injecting combustion air into the sampling train. Then inject combustion air into the sampling train, start the sample pump, and open the stack sample gas valve. Carry out these three operations within 15 to 30 seconds to avoid pressurizing the sampling train. Adjust the total sample flow rate to 2.0 ± 0.2 L/min (4.2 ± 0.4 ft³/hr). These flow rates produce an O_2 concentration of 5.0 percent in the stack gas, which must be maintained constantly to allow oxidation of reduced sulfur compounds to SO_2 . Adjust these flow rates during sampling as necessary. Monitor and record the combustion air manometer reading at regular intervals during the sampling period. Sample for 1 or 3 hours. At the end of sampling, turn off the sample pump and combustion air simultaneously (within 30 seconds of each other). All other procedures are the same as in Method 6, Section 8.3, except that the sampling train should not be purged. After collecting the sample, remove the probe from the stack and conduct a leak-check according to the procedures outlined in Section 8.2 of Method 6 (mandatory). After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see Section 8.5). After this system performance check and before the next test run, it is recommended that the probe be rinsed and brushed and the filter replaced.

Note: In Method 15, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 15A to be

consistent with Method 15, the following may be used to obtain a test run: (1) Collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Recover the hydrogen peroxide-containing impingers as detailed in Method 6, Section 8.4.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (before testing, optional) and (2) to validate a test run (after a run, mandatory). Perform a check in the field before testing consisting of at least two samples (optional), and perform an additional check after each 3-hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of COS and comparing the analyzed concentration with the known concentration. Mix the recovery gas with N_2 as shown in Figure 15A-4 if dilution is required. Adjust the flow rates to generate a COS concentration in the range of the stack gas or within 20 percent of the applicable standard at a total flow rate of at least 2.5 L/min (5.3 ft³/hr). Use Equation 15A-4 (see Section 12.5) to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow tube so that the diluted concentration of COS can be accurately calculated. Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the samples through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

8.5.3 The recovery check must be performed in the field before replacing the particulate filter and before cleaning the probe. A sample recovery of 100 ± 20 percent must be obtained for the data to be valid and should be reported with the emission data, but should not be used to correct the data. However, if the performance check results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test. Use Equation 15A-5 (see Section 12.6) to calculate the recovery efficiency.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensures validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration	Ensures accurate measurement of stack gas flow rate, sample volume
10.0	Barium standard solution standardization	Ensures precision of normality determination.
11.1	Replicate titrations	Ensures precision of titration determinations.
11.2	Audit sample analysis	Evaluates analyst's technique and standards preparation.

10.0 Calibration and Standardization

10.1 Metering System, Temperature Sensors, Barometer, and Barium Perchlorate Solution. Same as Method 6, Sections 10.1, 10.2, 10.4, and 10.5, respectively.

10.2 Rate Meter. Calibrate with a bubble flow tube.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, Sections 11.1 and 11.2.

11.2 Audit Sample Analysis. Same as Method 6, Section 11.3.

12.0 Data Analysis and Calculations

In the calculations, retain at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Nomenclature.

C_{COS} = Concentration of COS recovery gas, ppm.

$C_{RG(Act)}$ = Actual concentration of recovery check gas (after dilution), ppm.

$C_{RG(m)}$ = Measured concentration of recovery check gas generated, ppm.

C_{RS} = Concentration of reduced sulfur compounds as SO_2 , dry basis, corrected to standard conditions, ppm.

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{COS} = Flow rate of COS recovery gas, liters/min.

Q_N = Flow rate of diluent N_2 , liters/min.

R = Recovery efficiency for the system performance check, percent.

T_m = Average dry gas meter absolute temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

V_a = Volume of sample aliquot titrated, ml.

V_{ms} = Dry gas volume as measured by the sample train dry gas meter, liters.

V_{mc} = Dry gas volume as measured by the combustion air dry gas meter, liters.

$V_{ms(std)}$ = Dry gas volume measured by the sample train dry gas meter, corrected to standard conditions, liters.

$V_{mc(std)}$ = Dry gas volume measured by the combustion air dry gas meter, corrected to standard conditions, liters.

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample (average of replicate titrations), ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Calibration factor for sampling train dry gas meter.

Y_c = Calibration factor for combustion air dry gas meter.

32.03 = Equivalent weight of sulfur dioxide, mg/meq.

$$12025 \frac{\mu l}{meq} = \frac{(32.03 \text{ mg})}{meq} \frac{(24.051)}{mole} \frac{(mole)(lg)(10^3 \text{ ml})(10^3 \mu l)}{(64.06 \text{ g})(10^3 \text{ mg})(l)(ml)}$$

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_{ms} Y \frac{T_{std} P_{bar}}{T_m P_{std}} \quad \text{Eq. 15A-1}$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m}$$

Where:

$K_1 = 0.3855 \text{ } ^\circ\text{K/mm Hg}$ for metric units,

$= 17.65 \text{ } ^\circ\text{R/in. Hg}$ for English units.

12.3 Combustion Air Gas Volume, corrected to Standard Conditions.

$$V_{mc(std)} = K_1 Y_c \frac{(V_{mc})(P_{bar})}{T_m} \quad \text{Eq. 15A-2}$$

NOTE: Correct P_{bar} for the average pressure of the manometer during the sampling period.

12.4 Concentration of reduced sulfur compounds as ppm SO_2 .

$$C_{RS} = K_2 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{ms(std)} - V_{mc(std)}} \quad \text{Eq. 15A-3}$$

Where:

$$K_2 = 32.03 \frac{\text{mg}}{\text{meq}} \frac{24.05 \text{ l}}{\text{mole}} \frac{1 \text{ mole}}{64.06 \text{ g}} \frac{1 \text{ g}}{10^3 \text{ mg}} \frac{10^3 \text{ ml}}{1} \frac{10^3 \mu\text{l}}{1 \text{ ml}}$$

$$= \frac{12025 \text{ ml}}{\text{meq}}$$

12.5 Concentration of Generated Recovery Gas.

$$C_{\text{RG}} = \frac{(C_{\text{cos}})(Q_{\text{cos}})}{Q_{\text{cos}} + Q_{\text{N}_2}} \quad \text{Eq. 15A-4}$$

12.6 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{\text{RG(m)}}}{C_{\text{RG(act)}}} \times 100 \quad \text{Eq. 15A-5}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv when sampling at 2 lpm for 3 hours or 0.3 ppmv when sampling at 2 lpm for 1 hour. The upper concentration limit of the method exceeds concentrations of reduced sulfur compounds generally encountered in sulfur recovery plants.

13.2 Precision. Relative standard deviations of 2.8 and 6.9 percent have

been obtained when sampling a stream with a reduced sulfur compound concentration of 41 ppmv as SO₂ for 1 and 3 hours, respectively.

13.3 Bias. No analytical bias has been identified. However, results obtained with this method are likely to contain a positive bias relative to emission regulations due to the presence of nonregulated sulfur compounds (that are present in petroleum) in the emissions. The magnitude of this bias varies accordingly, and has not been quantified.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. American Society for Testing and Materials Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. Philadelphia, Pennsylvania. 1974. pp. 40–42.

2. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO₂ Scrubber Designs Used for TRS Monitoring. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York. Special Report 77–05. July 1977.

3. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. February 1980.

4. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York. Atmospheric Quality Improvement Technical Bulletin No. 81. October 1975.

5. Margeson, J.H., et al. A Manual Method for TRS Determination. Journal of Air Pollution Control Association. 35:1280–1286. December 1985.

BILLING CODE 6560–60–P

17.0 Tables, Diagrams, Flowcharts, and Validation Data

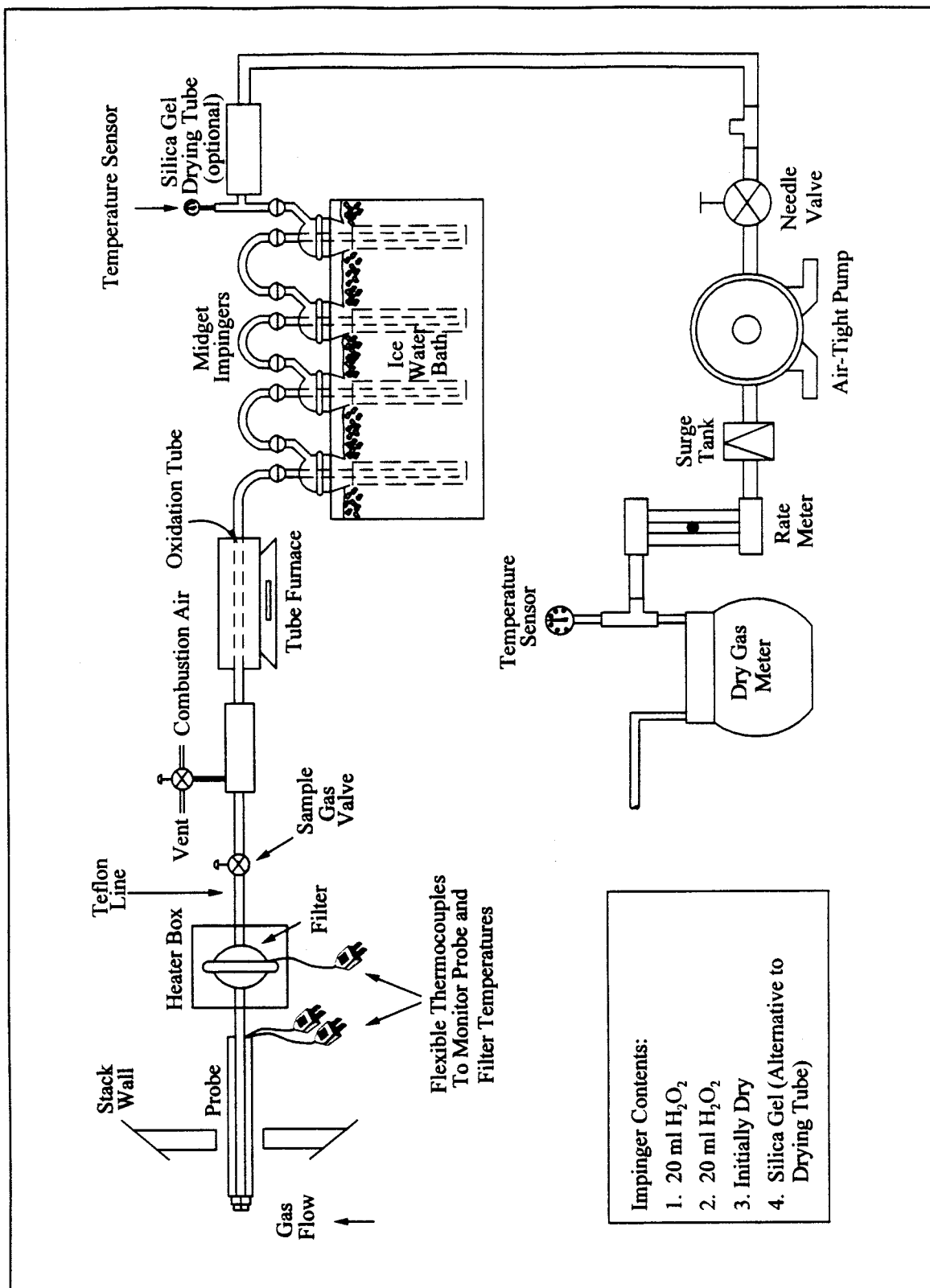


Figure 15A-1. Method 15A Sampling Train.

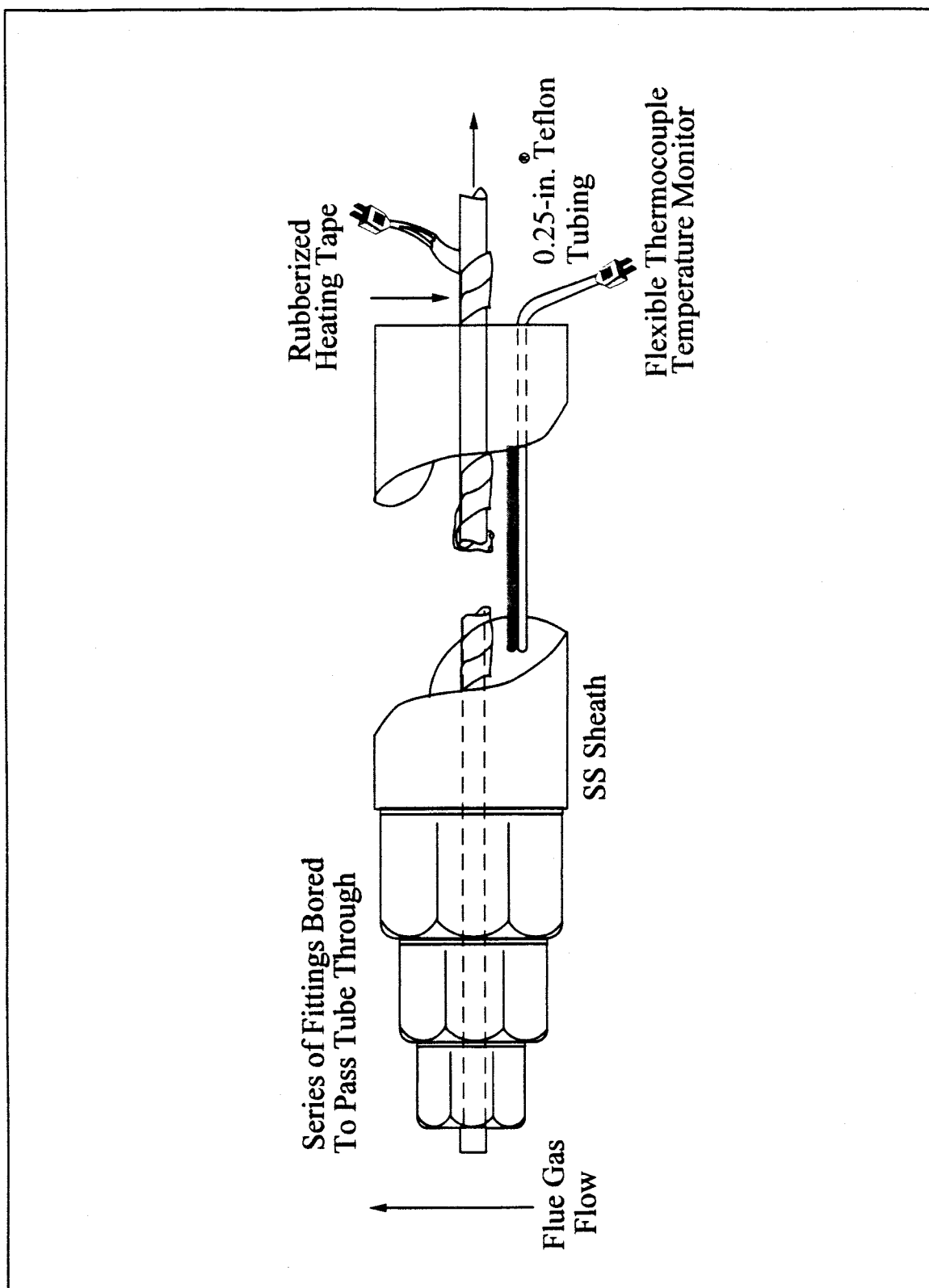


Figure 15A-2. Method 15A Sampling Probe.

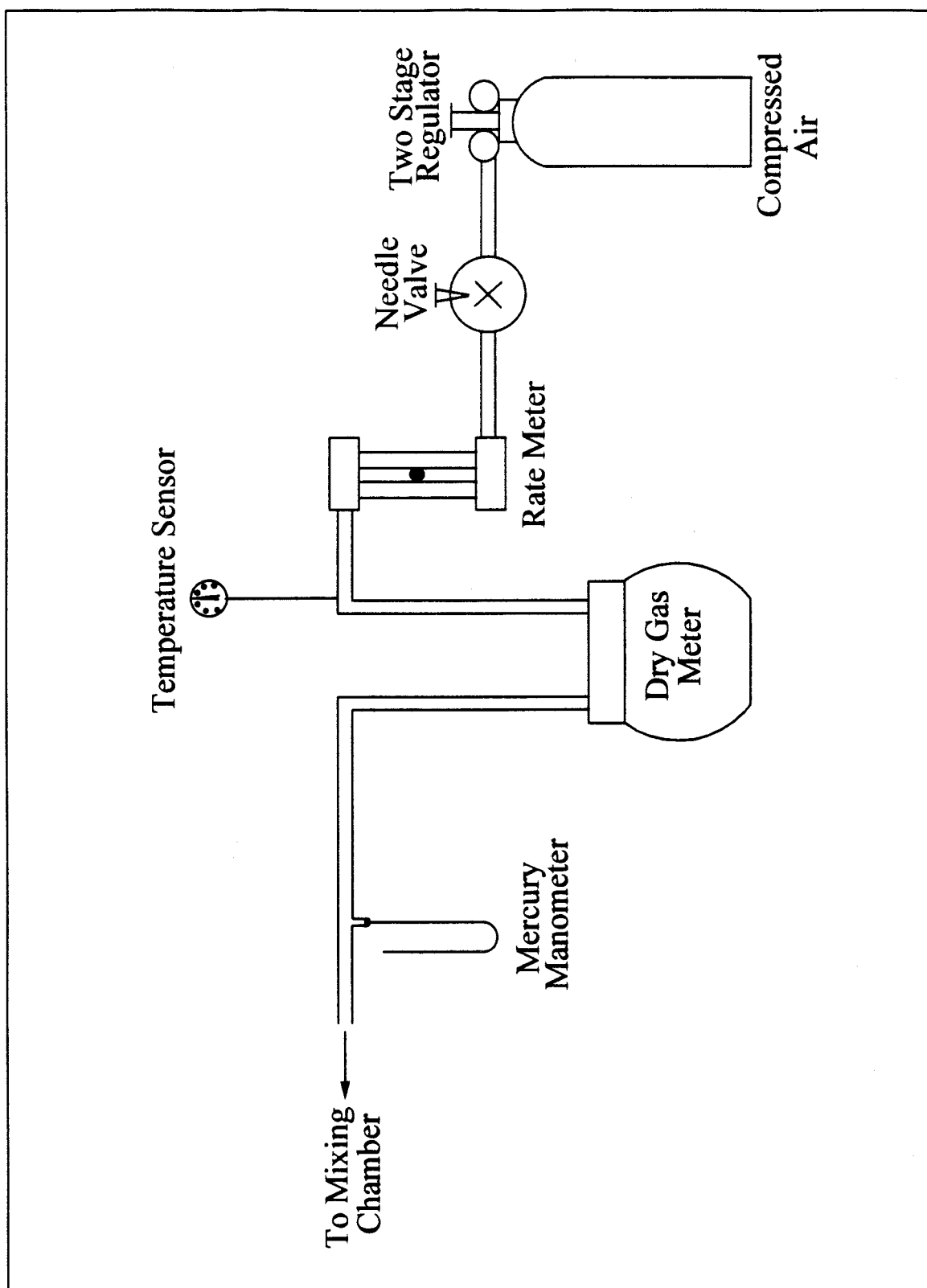


Figure 15A-3. Combustion Air Delivery System.

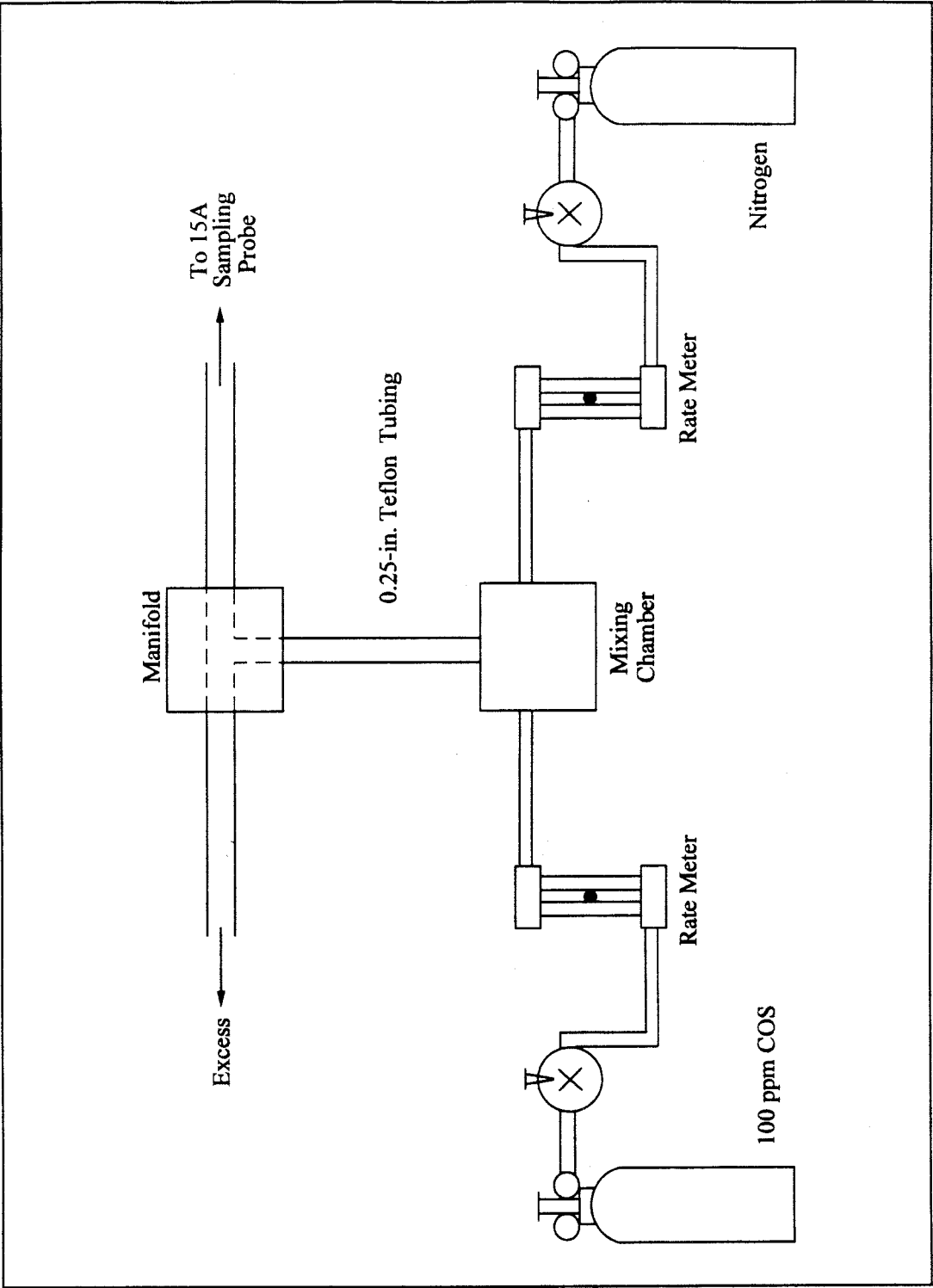


Figure 15A-4. Recovery Gas Generator System.

Method 16—Semicontinuous Determination of Sulfur Emissions From Stationary Sources

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge

of at least the following additional test methods: Method 1, Method 4, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Dimethyl disulfide [(CH ₃) ₂ S ₂]	62-49-20	50 ppb.
Dimethyl sulfide [(CH ₃) ₂ S]	75-18-3	50 ppb.
Hydrogen sulfide [H ₂ S]	7783-06-4	50 ppb.
Methyl mercaptan [CH ₄ S]	74-93-1	50 ppb.

1.2 Applicability. This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

Note: The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H₂S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as TRS.

3.0 Definitions. [Reserved]

4.0 Interferences

4.1 Moisture. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120 °C (248 °F). Moisture is removed in the SO₂ scrubber and heating the sample beyond this point is not necessary when the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the

GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO₂). CO and CO₂ have a substantial desensitizing effect on the flame photometric detector even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO₂ in the diluent gas. The CO₂ level should be approximately 10 percent for the case with CO₂ present. The two chromatograms should show agreement within the precision limits of Section 10.2.

4.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by using the Teflon filter after the probe.

4.4 Sulfur Dioxide (SO₂). Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest. The SO₂ scrubber described in Section 6.1.3 will effectively remove SO₂ from the sample.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide. A flammable, poisonous gas with the odor of rotten eggs. H₂S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous

membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1. Sample Collection. The following items are needed for sample collection.

6.1.1 Probe. Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It must be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes to reduce clogging of the filter and possible adsorption of sample gas. As an alternative, the probe described in Section 6.1.1 of Method 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

6.1.2 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Saville Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO₂ Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Saville.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (1/8 in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C (32 °F). The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the

effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO₂ scrubber must be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO₂ scrubber (or alternative point of moisture removal) must be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 1.3 cm (½ in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

6.1.5 Sample Pump. The sample pump must be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. Needed only for high sample concentrations. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

6.2.2 Gas Chromatograph. The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature ± 1 °C (2 °F).

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ± 1 °C (2 °F).

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10⁻⁹ to 10⁻⁴ amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.4.3 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped

with sample loop. Sample loop volumes must be chosen to provide the needed analytical range. Teflon tubing and fittings must be used throughout to present an inert surface for sample gas. The gas chromatograph must be calibrated with the sample loop used for sample analysis.

6.2.3 Gas Chromatogram Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H₂S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences. To demonstrate that adequate resolution has been achieved, submit a chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration. A calibration system, containing the following components, is required (see Figure 16-2).

6.3.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

6.3.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C (0.2 °F).

6.3.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within 1 °C (2 °F).

7.0 Reagents and Standards

7.1 Fuel. Hydrogen (H₂), prepurified grade or better.

7.2 Combustion Gas. Oxygen (O₂) or air, research purity or better.

7.3 Carrier Gas. Prepurified grade or better.

7.4 Diluent (if required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases

7.5.1 Permeation tubes, one each of H₂S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer and Sample Line Loss Gas. Same as Method 15, Sections 7.6 and 7.7.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 15, Section 8.0, except that the references to the dilution system may not be applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.0	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Same as Method 15, Section 10.0, with the following addition and exceptions:

10.1 Use the four compounds that comprise TRS instead of the three reduced sulfur compounds measured by Method 15.

10.2 Flow Meter. Calibration before each test run is recommended, but not required; calibration following each test series is mandatory. Calibrate each flow meter after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by 5 percent or more, the

completed test runs must be voided. Alternatively, the flow data that yield the lower flow measurement may be used. Flow over the permeation device may also be determined using a soap bubble flowmeter.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see Section 8.0).

12.0 Data Analysis and Calculations

12.1 Concentration of Reduced Sulfur Compounds. Calculate the average concentration of each of the four analytes (*i.e.*, DMDS, DMS, H₂S, and MeSH) over the sample run (specified in

Section 8.2 of Method 15 as 16 injections).

$$C = \frac{\sum_{i=1}^N S_i}{N} \quad \text{Eq. 16-1}$$

Where:

S_i = Concentration of any reduced sulfur compound from the *i*th sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12.2 TRS Concentration. Using Equation 16–2, calculate the TRS concentration for each sample run.

$$C_{\text{TRS}} = d \sum (C_{\text{H}_2\text{S}} + C_{\text{MeSH}} + C_{\text{DMS}} + 2C_{\text{DMDS}}) \quad \text{Eq. 16-2}$$

Where:

C_{TRS} = TRS concentration, ppmv.

C_{H₂S} = Hydrogen sulfide concentration, ppmv.

C_{MeSH} = Methyl mercaptan concentration, ppmv.

C_{DMS} = Dimethyl sulfide concentration, ppmv.

C_{DMDS} = Dimethyl disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

12.3 Average TRS Concentration.

Calculate the average TRS concentration for all sample runs performed.

$$\text{Average TRS} = \frac{\sum_{i=1}^n \text{TRS}_i}{N(1 - B_{\text{wo}})} \quad \text{Eq. 16-3}$$

Where:

Average TRS = Average total reduced sulfur in ppm.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16–2.

N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases.

13.0 Method Performance

13.1 Analytical Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10- to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases.

13.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

14.0 Pollution Prevention. [Reserved]**15.0 Waste Management. [Reserved]****16.0 References**

1. O'Keeffe, A.E., and G.C. Ortman. "Primary Standards for Trace Gas Analysis." *Analytical Chemical Journal*, 38,76. 1966.
2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur

Compounds at Sub-Part-Per-Million Levels." *Environmental Science and Technology*, 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6–8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." *Pulp and Paper Magazine of Canada*, 73,3. March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting, St. Louis, MO. June 14–19, 1970.

6. General Reference. *Standard Methods of Chemical Analysis*, Volumes III–A and III–B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

BILLING CODE 6560–50–P

17.0 Tables, Diagrams, Flowcharts, and Validation Data

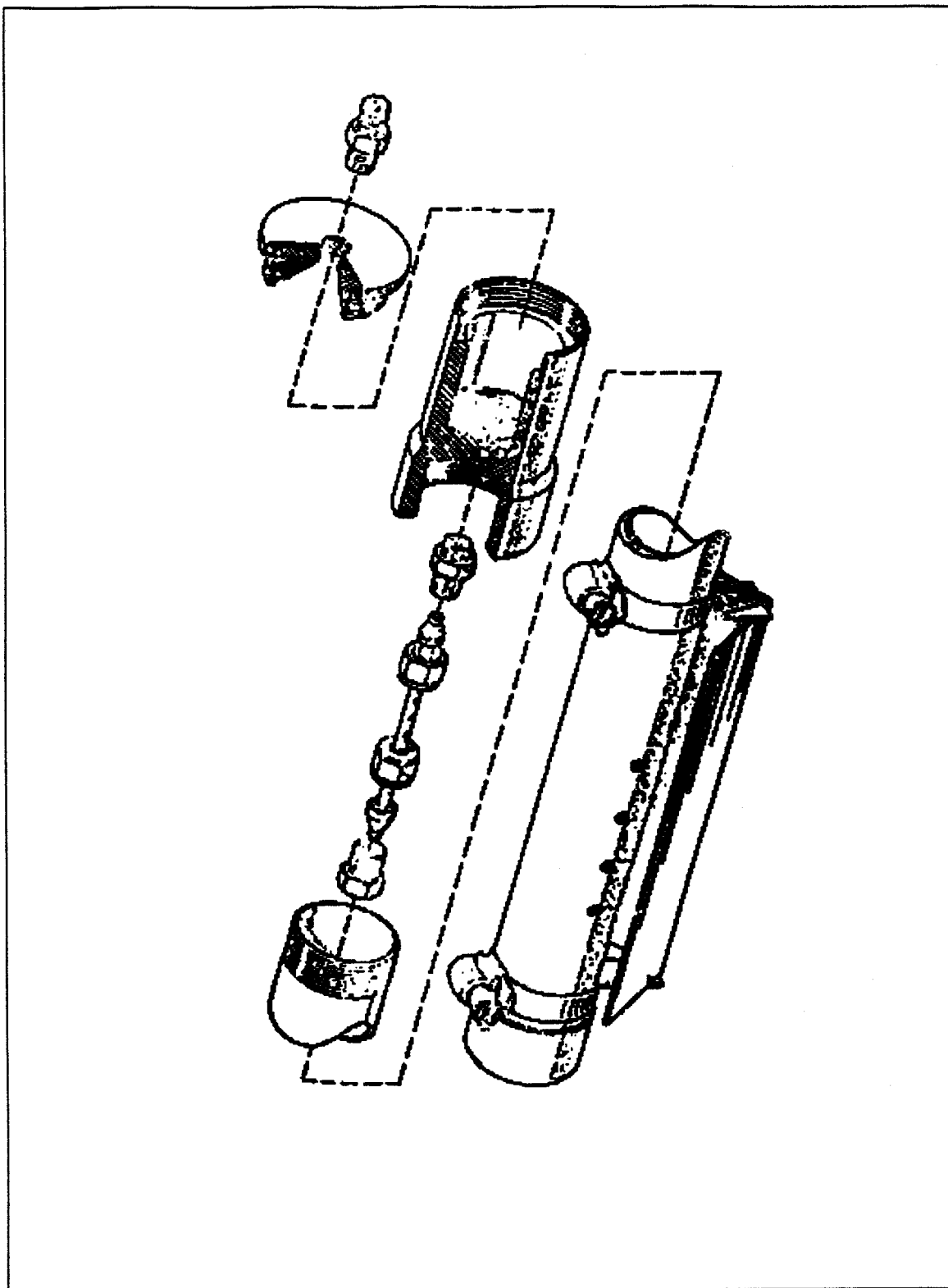


Figure 16-1. Probe used for Sample Gas Containing High Particulate Matter Loading.

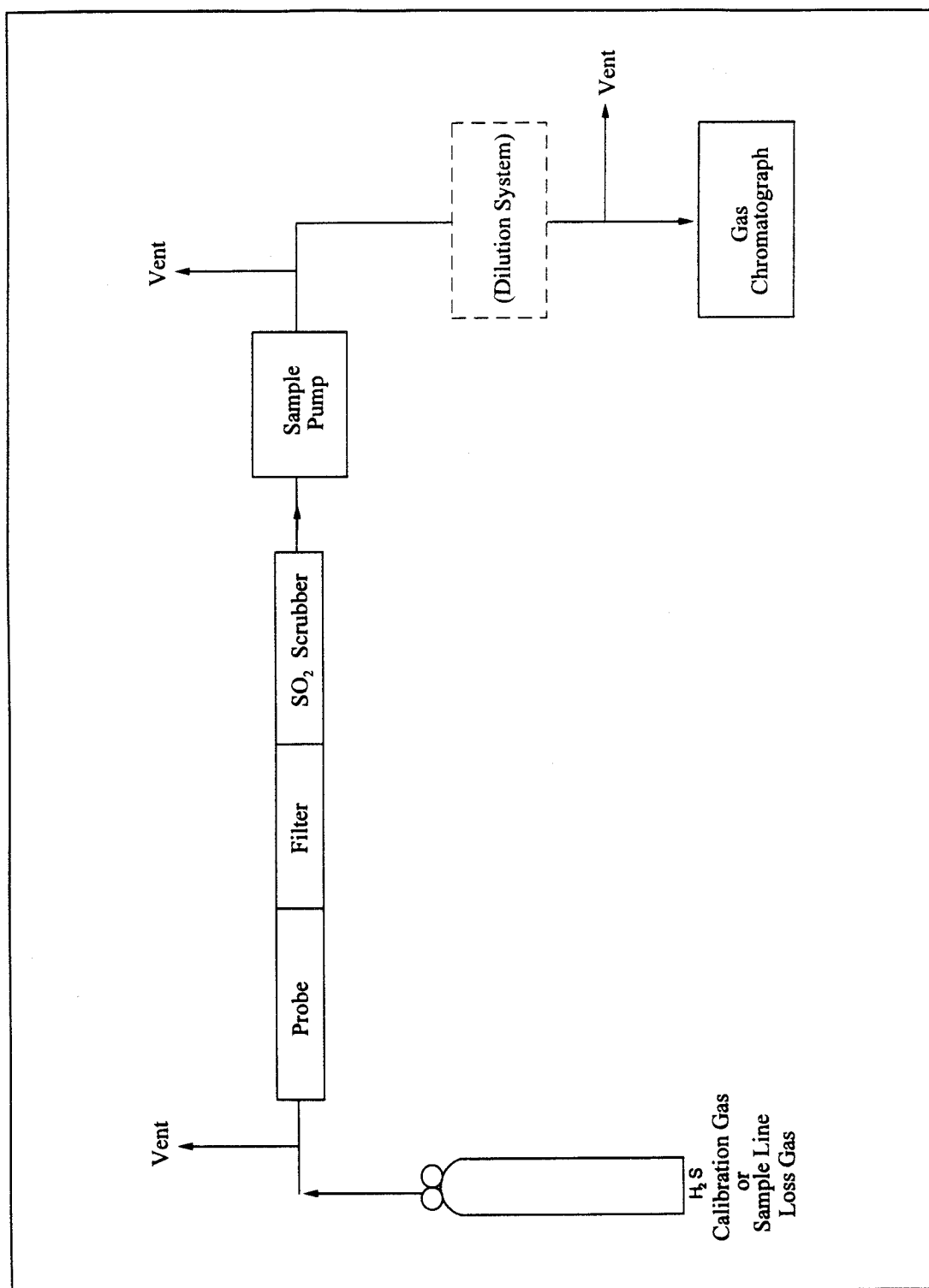


Figure 16-2. Calibration System.

Method 16A—Determination of Total Reduced Sulfur Emissions From Stationary Sources (Impinger Technique)

Note: This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Total reduced sulfur (TRS) including:	N/A	See Section 13.1.
Dimethyl disulfide [(CH ₃) ₂ S ₂]	62-49-20	
Dimethyl sulfide [(CH ₃) ₂ S]	75-18-3	
Hydrogen sulfide [H ₂ S]	7783-06-4	
Methyl mercaptan [CH ₄ S]	74-93-1	
Reduced sulfur (RS) including:	N/A	
H ₂ S	7783-06-4	
Carbonyl sulfide [COS]	463-58-1	
Carbon disulfide [CS ₂]	75-15-0	
Reported as: Sulfur dioxide (SO ₂)	7449-09-5	

1.2 **Applicability.** This method is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills, reduced sulfur compounds (H₂S, carbonyl sulfide, and carbon disulfide) from sulfur recovery units at onshore natural gas processing facilities, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO₂.

1.3 **Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. SO₂ is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO₂, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

3.0 Definitions. [Reserved]**4.0 Interferences**

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO₂ and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H₂S to be absorbed prior to oxidation. Furthermore, if the calcium carbonate enters the hydrogen peroxide impingers,

the calcium will precipitate sulfate ion. Proper use of the particulate filter described in Section 6.1.3 will eliminate this interference.

5.0 Safety

5.1 **Disclaimer.** This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 **Corrosive reagents.** The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 **Hydrogen Peroxide (H₂O₂).** Irritating to eyes, skin, nose, and lungs.

5.2.2 **Sodium Hydroxide (NaOH).** Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 **Sulfuric Acid (H₂SO₄).** Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m³ will cause lung damage in uninitiated. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 **Hydrogen Sulfide (H₂S).** A flammable, poisonous gas with the odor

of rotten eggs. H₂S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 **Sample Collection.** The sampling train is shown in Figure 16A-1 and component parts are discussed below. Modifications to this sampling train are acceptable provided the system performance check is met (see Section 8.5).

6.1.1 **Probe.** Teflon tubing, 6.4-mm (¼-in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device should be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼-in.) Teflon elbow (bored out) should be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A-2.

6.1.2 **Probe Brush.** Nylon bristle brush with handle inserted into a 3.2-mm (⅛-in.) Teflon tubing. The Teflon tubing should be long enough to pass

the brush through the length of the probe.

6.1.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2- μ m porosity, Teflon filter (available through Saville Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.1.4 SO₂ Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Saville.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm ($\frac{1}{8}$ -in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.1.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm ($\frac{1}{4}$ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90-degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 \pm 100 °C (1472 \pm 180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.1.7 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as Method 6, Sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midjet bubbler of Method 6, Section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge.

6.1.9 Rate Meter. Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of approximately 2 liters/min (4.2 ft³/hr).

6.1.10 Volume Meter. Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 liters/min (4.2 ft³/hr) with an accuracy of 2 percent.

6.2 Sample Recovery. Polyethylene Bottles, 250-ml (one per sample).

6.3 Sample Preparation and Analysis. Same as Method 6, Section 6.3, except a 10-ml buret with 0.05-ml graduations is required, and the spectrophotometer is not needed.

7.0 Reagents and Standards

Note: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Sample Collection. The following reagents are required for sample analysis:

7.1.1 Water. Same as in Method 6, Section 7.1.1.

7.1.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.1.3 Hydrogen Peroxide, 3 percent. Same as in Method 6, Section 7.1.3 (40 ml is needed per sample).

7.1.4 Recovery Check Gas. Hydrogen sulfide (100 ppmv or less) in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11 or by gas chromatography where the instrument is calibrated with an H₂S permeation tube as described below. For Method 11, the relative standard deviation should not exceed 5 percent on at least three 20-minute runs.

Note: Alternatively, hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (6.4 ft³/hr), an H₂S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

7.1.5 Combustion Gas. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: Diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Flow from a compressed air cylinder is also acceptable.

7.2 Sample Recovery and Analysis. Same as Method 6, Sections 7.2.1 and 7.3, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train.

8.1.1 For the SO₂ scrubber, measure 100 ml of citrate buffer into the first and

second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor.

8.1.2 For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midjet impingers. Leave the third midjet impinger empty, and place silica gel in the fourth midjet impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Maintain the oxidation furnace at 800 \pm 100 °C (1472 \pm 180 °F). Place crushed ice and water around all impingers.

8.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers and bypassing all other sampling train components. A purge rate of 2 liters/min for 10 minutes has been found to be sufficient to obtain equilibrium. After the citrate scrubber has been conditioned, assemble the sampling train, and conduct (optional) a leak-check as described in Method 6, Section 8.2.

8.3 Sample Collection. Same as in Method 6, Section 8.3, except the sampling rate is 2 liters/min (\pm 10 percent) for 1 or 3 hours. After the sample is collected, remove the probe from the stack, and conduct (mandatory) a post-test leak-check as described in Method 6, Section 8.2. The 15-minute purge of the train following collection should not be performed. After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see Section 8.5) to determine the reduced sulfur recovery efficiency through the sampling train. After this system performance check and before the next test run, rinse and brush the probe with water, replace the filter, and change the citrate scrubber (optional but recommended).

Note: In Method 16, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 16A to be consistent with Method 16, the following may be used to obtain a test run: (1) collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Disconnect the impingers. Quantitatively transfer the contents of the midjet impingers of the Method 6 part of the train into a leak-free polyethylene bottle for

shipment. Rinse the three midget impingers and the connecting tubes with water and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (prior to testing; optional) and (2) to validate a test run (after a run). Perform a check in the field prior to testing consisting of at least two samples (optional), and perform an additional check after each 3 hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of H₂S and comparing the analyzed concentration with the known concentration. Mix the

H₂S recovery check gas (Section 7.1.4) and combustion gas in a dilution system such as that shown in Figure 16A-3. Adjust the flow rates to generate an H₂S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft³/hr). Use Equation 16A-3 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow meter so that the diluted concentration of H₂S can be accurately calculated.

8.5.3 Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or some other suitable

device that will ensure extraction of a representative sample.

8.5.4 The recovery check must be performed in the field prior to replacing the SO₂ scrubber and particulate filter and before the probe is cleaned. Use Equation 16A-4 (see Section 12.5) to calculate the recovery efficiency. Report the recovery efficiency with the emission data; do not correct the emission data for the recovery efficiency. A sample recovery of 100 ± 20 percent must be obtained for the emission data to be valid. However, if the recovery efficiency is not in the 100 ± 20 percent range but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensure validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Barium standard solution standardization	Ensure precision of normality determination.
11.1	Replicate titrations	Ensure precision of titration determinations.
11.2	Audit sample analysis	Evaluate analyst's technique and standards preparation.

10.0 Calibration

Same as Method 6, Section 10.0.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, Sections 11.1 and 11.2, respectively, with the following exception: for 1-hour sampling, take a 40-ml aliquot, add 160 ml of 100 percent isopropanol and four drops of thorin.

11.2 Audit Sample Analysis. Same as Method 6, Section 11.3.

12.0 Data Analysis and Calculations

In the calculations, at least one extra decimal figure should be retained beyond that of the acquired data. Figures should be rounded off after final calculations.

12.1 Nomenclature.

C_{TRS} = Concentration of TRS as SO₂, dry basis corrected to standard conditions, ppmv.

C_{RG(act)} = Actual concentration of recovery check gas (after dilution), ppm.

C_{RG(m)} = Measured concentration of recovery check gas generated, ppm.

C_{H₂S} = Verified concentration of H₂S recovery gas.

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{H₂S} = Calibrated flow rate of H₂S recovery gas, liters/min.

Q_{CG} = Calibrated flow rate of combustion gas, liters/min.

R = Recovery efficiency for the system performance check, percent.

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, liters (dcf).

V_{m(std)} = Dry gas volume measured by the dry gas meter, corrected to standard conditions, liters (dscf).

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

32.03 = Equivalent weight of sulfur dioxide, mg/meq.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_m Y \frac{T_{std} P_{bar}}{T_m P_{std}} \quad \text{Eq. 16A-1}$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m}$$

Where:

K₁ = 0.3855 °K/mm Hg for metric units, = 17.65 °R/in. Hg for English units.

12.3 Concentration of TRS as ppm SO₂.

$$C_{TRS} = K_2 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}} \quad \text{Eq. 16A-2}$$

Where:

$$K_2 = 32.03 \frac{\text{mg}}{\text{meq}} \frac{24.05\text{L}}{\text{mole}} \frac{1\text{mole}}{64.06\text{g}} \frac{1\text{g}}{10^3\text{mg}} \frac{10^3\text{mL}}{\text{L}} \frac{10^3\mu\text{L}}{\text{mL}}$$

$$= \frac{12025\mu\text{L}}{\text{meq}}$$

12.4 Concentration of Recovery Gas Generated in the System Performance Check.

$$C_{\text{RG}} = \frac{Q_{\text{H}_2\text{S}} C_{\text{H}_2\text{S}}}{Q_{\text{H}_2\text{S}} + Q_{\text{CG}}} \quad \text{Eq. 16A-3}$$

12.5 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{\text{RG(m)}}}{C_{\text{RG(act)}}} \times 100 \quad \text{Eq. 16A-4}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv SO₂ when sampling at 2 liters/min (4.2 ft³/hr) for 3 hours or 0.3 ppmv when sampling at 2 liters/min (4.2 ft³/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision. Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

13.3 Bias.

13.3.1 No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16 at a lime kiln indicated that there was no bias in Method 16A. However, instability of the source emissions adversely affected the comparison. The precision of Method 16A at the lime kiln was similar to that obtained at the recovery boiler (Section 13.2.1).

13.3.3 Relative standard deviations of 2.7 and 7.7 percent have been obtained for system performance checks.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures

As an alternative to the procedures specified in Section 7.1.4, the following procedure may be used to verify the H₂S concentration of the recovery check gas.

16.1 Summary. The H₂S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range. The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences. There are no known interferences to this procedure when used to analyze cylinder gases containing H₂S in nitrogen.

16.4 Precision and Bias. Laboratory tests have shown a relative standard deviation of less than 3 percent. The procedure showed no bias when compared to a gas chromatographic method that used gravimetrically certified permeation tubes for calibration.

16.5 Equipment and Supplies.

16.5.1 Sampling Apparatus. The sampling train is shown in Figure 16A-4. Its component parts are discussed in Sections 16.5.1.1 through 16.5.2.

16.5.1.1 Sampling Line. Teflon tubing (1/4-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve. Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers. Three impingers of approximately 100-ml capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The impinger bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 6.4-mm (1/4-in.) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1.27 cm (1/2 in.) from the bottom (Southern Scientific, Inc., Micanopy, Florida; Set Number S6962-048). The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer. Same as Method 11, Sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator. Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter. Calibrated for 100 and 500 ml, or two separate bubble meters.

16.5.1.7 Critical Orifice. For volume and rate measurements. The critical orifice may be fabricated according to Section 16.7.3 and must be calibrated as specified in Section 16.12.4.

16.5.1.8 Graduated Cylinder. 50-ml size.

16.5.1.9 Volumetric Flask. 1-liter size.

16.5.1.10 Volumetric Pipette. 15-ml size.

16.5.1.11 Vacuum Gauge. Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch.

16.5.2 Sample Recovery and Analysis.

16.5.2.1 Erlenmeyer Flasks. 125- and 250-ml sizes.

16.5.2.2 Pipettes. 2-, 10-, 20-, and 100-ml volumetric.

16.5.2.3 Burette. 50-ml size.

16.5.2.4 Volumetric Flask. 1-liter size.

16.5.2.5 Graduated Cylinder. 50-ml size.

16.5.2.6 Wash Bottle.

16.5.2.7 Stirring Plate and Bars.

16.6 Reagents and Standards. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

16.6.1 Water. Same as Method 11, Section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution. Dissolve 20 g zinc acetate in water, and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [KH(IO₃)₂] Solution, Standard 0.100 N. Dissolve 3.249 g anhydrous KH(IO₃)₂ in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate (Na₂S₂O₃) Solution, Standard 0.1 N. Same as Method 11, Section 7.3.2. Standardize according to Section 16.12.2.

16.6.5 Na₂S₂O₃ Solution, Standard 0.01 N. Pipette 100.0 ml of 0.1 N Na₂S₂O₃ solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N. Same as Method 11, Section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N. Same as in Method 11, Section 7.2.4. Standardize according to Section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight. Add 230 ml concentrated HCl (specific gravity 1.19) to 770 ml water.

16.6.9 Starch Indicator Solution. To 5 g starch (potato, arrowroot, or soluble), add a little cold water, and grind in a mortar to a thin paste. Pour into 1 liter of boiling water, stir, and let settle overnight. Use the clear supernatant. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium

azide per liter of starch solution. Some commercial starch substitutes are satisfactory.

16.7 Pre-test Procedures.

16.7.1 Selection of Gas Sample Volumes. This procedure has been validated for estimating the volume of cylinder gas sample needed when the H₂S concentration is in the range of 5 to 1500 ppmv. The sample volume ranges were selected in order to ensure a 35 to 60 percent consumption of the 20 ml of 0.01 N iodine (thus ensuring a 0.01 N Na₂S₂O₃ titer of approximately 7 to 12 ml). The sample volumes for various H₂S concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the H₂S concentration stated by the manufacturer. For example, for analyzing a cylinder gas containing

approximately 10 ppmv H₂S, the optimum sample volume is 65 liters (650 ppm-liters/10 ppmv). For analyzing a cylinder gas containing approximately 1000 ppmv H₂S, the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppmv).

Approximate cylinder gas H ₂ S concentration (ppmv)	Approximate ppm-liters desired
5 to <30	650
30 to <500	800
500 to <1500	1000

16.7.2 Critical Orifice Flow Rate Selection. The following table shows the ranges of sample flow rates that are desirable in order to ensure capture of H₂S in the impinger solution. Slight deviations from these ranges will not

have an impact on measured concentrations.

Cylinder gas H ₂ S concentration (ppmv)	Critical orifice flow rate (ml/min)
5 to 50 ppmv	1500 ± 500
50 to 250 ppmv	500 ± 250
250 to <1000 ppmv	200 ± 50
>1000 ppmv	75 ± 25

16.7.3 Critical Orifice Fabrication. Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting 1/16-in. x 1/4-in. (0.16 cm x 0.64 cm) reducing fittings to both ends. The inside diameters and lengths of orifice tubes needed to obtain specific flow rates are shown below.

Tube (in. OD)	Tube (in. ID)	Length (in.)	Flowrate (ml/min)	Altech Catalog No.
1/16	0.007	1.2	85	301430
1/16	0.01	3.2	215	300530
1/16	0.01	1.2	350	300530
1/16	0.02	1.2	1400	300230

16.7.4 Determination of Critical Orifice Approximate Flow Rate. Connect the critical orifice to the sampling system as shown in Figure 16A-4 but without the H₂S cylinder. Connect a rotameter in the line to the first impinger. Turn on the pump, and adjust the valve to give a reading of

about half atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable flow rate is reached, and record this as the critical vacuum. The measured flow rate indicates the expected critical flow rate of the orifice. If this flow rate is in the range shown in Section 16.7.2, proceed

with the critical orifice calibration according to Section 16.12.4.

16.7.5 Determination of Approximate Sampling Time. Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in Section 16.7.1.

$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A-4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A-4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut,

to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in Section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve

followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N Na₂S₂O₃ until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

Note: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30 to 45 seconds after the titration endpoint is reached. This should not be taken to mean